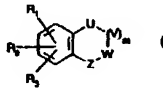
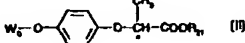
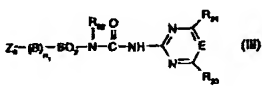
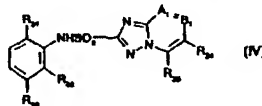
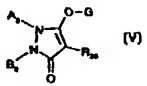
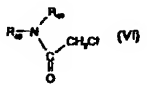
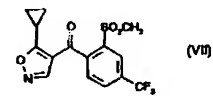




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| <p>(54) Title: HERBICIDAL COMPOSITION</p> | | |
| <p>(57) Abstract</p> <p>The present invention relates to new compounds of formula (I) wherein R₁ to R₃, U, V, W, Z and m have the significances given in the description, their use as antidotes in herbicidal compositions for the control of weeds and grasses in useful plant cultivations, as well as compositions having selective herbicide activity, which contain the compound of formula (I), and as herbicides the compounds of formulae (II) to (VII) wherein W₀, R₂₁, Z₀, B, n₁, R₂₂-R₂₄, E, R₃₁-R₃₅, A₁, B₁, A₂, B₂, R₃₆, G, R₄₈ and R₄₉ have the significances given in the description.</p> <div style="display: flex; justify-content: space-around; align-items: flex-start;"> <div style="text-align: center;">  <p>(I)</p> </div> <div style="text-align: center;">  <p>(II)</p> </div> <div style="text-align: center;">  <p>(III)</p> </div> <div style="text-align: center;">  <p>(IV)</p> </div> <div style="text-align: center;">  <p>(V)</p> </div> <div style="text-align: center;">  <p>(VI)</p> </div> <div style="text-align: center;">  <p>(VII)</p> </div> </div> | | |

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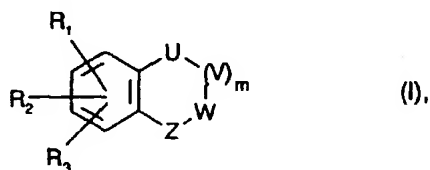
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Herbicide composition

The present invention relates to new antidotes, their use as antidotes in herbicidal compositions, these compositions and their usage in the control of grasses and weeds in cultivations of useful plants, especially in cultivations of maize, cereals, soybeans and rice.

The objects of the present invention are compounds of formula I



wherein

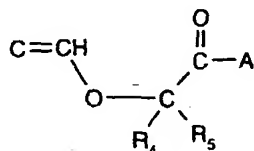
R₁ is hydrogen, C₁-C₄-alkyl, C₁-C₄-alkyl substituted by C₁-C₄-alkyl-X- or C₁-C₄-halogen-alkyl-X-, C₁-C₄-halogen-alkyl, nitro, cyano, -COOR₆, -NR₉R₁₀, -SO₂NR₁₁R₁₂ or -CONR₁₃R₁₄;

R₂ is hydrogen, halogen, C₁-C₄-alkyl, trifluoromethyl, C₁-C₄-alkoxy or C₁-C₄-halogen-alkoxy;

R₃ is hydrogen, halogen or C₁-C₄-alkyl;

U, V, W and Z, independently of one another, are oxygen, sulphur, C(R₁₅)R₁₆, carbonyl, NR₁₇ or

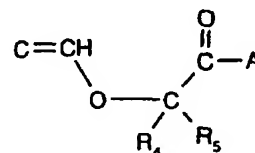
a group



with the provisos that

a) at least one of the ring members U, V, W or Z is carbonyl, and one ring member which

is adjacent to this or these ring members signifies the group



whereby this group only appears once; and

b) two adjacent ring members U and V, V and W and W and Z cannot simultaneously signify oxygen;

R₄ and R₅, independently of one another, signify hydrogen or C₁-C₈-alkyl; or

R₄ and R₅ together form a C₂-C₆-alkylene group;

A is R₇-Y- or -NR₁₈R₁₉;

X is oxygen or -S(O)_p;

Y is oxygen or sulphur;

R₇ is hydrogen, C₁-C₈-alkyl, C₁-C₈-halogen-alkyl, C₁-C₄-alkoxy-C₁-C₈-alkyl, C₃-C₆-alkenyloxy-C₁-C₈-alkyl or phenyl-C₁-C₈-alkyl, whereby the phenyl ring may be substituted by halogen, C₁-C₄-alkyl, trifluoromethyl, methoxy or methyl-S(O)_p; C₃-C₆-alkenyl, C₃-C₆-halogen-alkenyl, phenyl-C₃-C₆-alkenyl, C₃-C₆-alkinyl, phenyl-C₃-C₆-alkinyl, oxetanyl, furfuryl or tetrahydrofurfuryl;

R₈ is hydrogen or C₁-C₄-alkyl;

R₉ is hydrogen, C₁-C₄-alkyl or C₁-C₄-alkylcarbonyl;

R₁₀ is hydrogen or C₁-C₄-alkyl; or

R₉ and R₁₀ together form a C₄- or C₅-alkylene group;

R₁₁, R₁₂, R₁₃ and R₁₄, independently of one another, are hydrogen or C₁-C₄-alkyl; or R₁₁, together with R₁₂ or R₁₃ together with R₁₄, independently of one another, are C₄- or C₅-alkylene, whereby one carbon atom may be replaced by oxygen or sulphur, or one or two carbon atoms may be replaced by -NR₁₅;

R₁₅ and R₁₆, independently of one another, are hydrogen or C₁-C₈-alkyl; or

R₁₅ and R₁₆ together are C₂-C₆-alkylene;

R₁₇ is hydrogen, C₁-C₈-alkyl, optionally substituted phenyl or benzyl optionally substituted on the phenyl ring;

R₁₈ is hydrogen, C₁-C₈-alkyl, phenyl, phenyl-C₁-C₈-alkyl, whereby the phenyl rings may be substituted by fluorine, chlorine, bromine, nitro, cyano, -OCH₃, C₁-C₄-alkyl or CH₃SO₂; C₁-C₄-alkoxy-C₁-C₈-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkinyl or C₃-C₆-cycloalkyl;

R₁₉ is hydrogen, C₁-C₈-alkyl, C₃-C₆-alkenyl or C₃-C₆-alkinyl; or

R₁₈ and R₁₉ together are C₄- or C₅-alkylene, whereby one carbon atom may be replaced by oxygen or sulphur, or one or two carbon atoms may be replaced by -NR₂₀;

R₂₀ is hydrogen or C₁-C₄-alkyl;

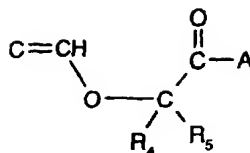
m is 0 or 1; and

p signifies 0, 1 or 2,

as well as agronomically compatible salts and stereoisomers of these compounds.

The proviso a) denotes compounds of formula I, wherein 1, 2 or 3 of the ring members U, V, W and/or Z, independently of one another, are carbonyl, and one ring member which is adjacent

thereto is the group



This group itself appears

only once in the compound of formula I. Therefore, in the proviso a), "one" is the numeral.

In the above-mentioned definitions, halogen is understood to be iodine and preferably fluorine, chlorine and bromine.

The alkyl, alkenyl and alkynyl groups appearing in the definitions of the substituents may be straight-chain or branched, and the same applies also to the alkyl, alkenyl and alkynyl moiety of the alkylcarbonyl, alkoxyalkyl, alkylthio and alkylsulphonyl groups.

Alkyl groups denote for example methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec.-butyl, iso-butyl, tert.-butyl, as well as the various isomeric pentyl, hexyl, heptyl and octyl radicals. Methyl, ethyl, n-propyl, iso-propyl and n-butyl are preferred.

Examples of alkenyls which may be mentioned are allyl, methallyl, 1-methylvinyl, but-2-en-1-yl, pentenyl and 2-hexenyl, preferably alkenyl radicals with a chain length of 3 to 5 carbon atoms.

Examples of alkynyls which may be mentioned are propargyl, 1-methylpropargyl, 3-butenyl, but-2-in-1-yl, 2-methylbut-3-in-2-yl, but-3-in-2-yl, 1-pentynyl, pent-4-in-1-yl and 2-hexynyl, preferably alkynyl radicals with a chain length of 3 to 5 carbon atoms.

The halogen-alkyl which may be considered are alkyl groups that are substituted by halogen once or many times, especially once to three times, whereby halogen signifies in detail iodine and especially fluorine, chlorine and bromine, for example fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2-chloroethyl, 2,2-dichloroethyl, 2,2,2-trifluoroethyl and 2,2,2-trichloroethyl.

Alkylsulphonyl is for example methylsulphonyl, ethylsulphonyl, propylsulphonyl, isopropylsulphonyl, n-butylsulphonyl, iso-butylsulphonyl, sec.-butylsulphonyl and tert.-butylsulphonyl; preferably methylsulphonyl and ethylsulphonyl.

Halogen-alkylsulphonyl is for example fluoromethylsulphonyl, difluoromethylsulphonyl, trifluoromethylsulphonyl, chloromethylsulphonyl, trichloromethylsulphonyl, 2-fluoroethylsulphonyl, 2,2,2-trifluoroethylsulphonyl and 2,2,2-trichloroethylsulphonyl.

Alkylcarbonyl is especially acetyl and propionyl.

Alkoxy is for example methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, iso-butoxy, sec.-butoxy and tert.-butoxy.

Alkenyloxy is for example allyloxy, methallyloxy and but-2-en-1-yloxy.

Alkinyloxy is for example propargyloxy and 1-methylpropargyloxy.

Alkoxyalkyl is for example methoxymethyl, methoxyethyl, ethoxymethyl, ethoxyethyl, n-propoxymethyl, n-propoxyethyl, iso-propoxymethyl and iso-propoxyethyl.

Halogenalkoxy is for example fluoromethoxy, difluoromethoxy, trifluoromethoxy, 2,2,2-trifluoroethoxy, 1,1,2,2-tetrafluoroethoxy, 2-fluoroethoxy, 2-chloroethoxy and 2,2,2-trichloroethoxy.

Of the alkenyl radicals that are substituted 1, 2 or 3 times by halogen, preference is given to those which have a chain length of 3 or 4 carbon atoms. The alkenyloxy groups may be substituted by halogen at saturated or unsaturated carbon atoms.

The halogen-alkenyloxy which may be considered are alkenyloxy groups that are substituted by halogen once or many times, whereby halogen signifies in detail bromine, iodine and especially fluorine and chlorine, for example 2- and 3-fluoropropenyloxy, 2- and 3-chloropropenyloxy, 2- and 3-bromopropenyloxy, 2,3,3-trifluoropropenyloxy, 2,3,3-trichloropropenyloxy, 4,4,4-trifluoro-but-2-en-1-yloxy and 4,4,4-trichloro-but-2-en-1-yloxy.

Alkylthio signifies for example methylthio, ethylthio, propylthio and butylthio, as well as the branched isomers thereof.

Phenyl or benzyl per se, or as part of a substituent, such as phenylalkyl or benzylamino, exist in optionally substituted form, in which case the substituents may be in ortho-, meta- or para-position. Substituents are e.g. C₁-C₄-alkyl, C₁-C₄-alkoxy, halogen, C₁-C₄-halogen-alkyl or C₁-C₄-halogen-alkoxy.

Corresponding significances may also be assigned to the substituents in compound definitions, such as alkyl-Y, halogen-alkyl-Y, alkoxy-alkyl-Y, alkenyloxy-alkyl-Y, phenyl-alkyl-Y, alkenyl-Y, halogen-alkenyl-Y, phenyl-alkenyl-Y, phenyl-alkinyl-Y, halogen-alkyl-X-alkyl and alkyl-S(O)-alkyl.

In the definition of alkylcarbonyl, the carbonyl carbon atom is not included in the lower and upper numeric limits for carbon atoms respectively indicated.

Preference is given to compounds of formula I, wherein R_{17} is hydrogen or C_1 - C_8 -alkyl, and R_{18} is hydrogen, C_1 - C_8 -alkyl, phenyl, phenyl- C_1 - C_8 -alkyl, whereby the phenyl rings may be substituted by fluorine, chlorine, bromine, nitro, cyano, $-OCH_3$, C_1 - C_4 -alkyl or CH_3SO_2 ; C_1 - C_4 -alkoxy- C_1 - C_8 -alkyl, C_3 - C_6 -alkenyl or C_3 - C_6 -alkinyl.

Preference is similarly given to compounds of formula I, wherein R_4 and R_5 are hydrogen.

Preference is also given to compounds of formula I, wherein A is R_7 -Y-.

Of these compounds, preference is given in particular to those in which Y is oxygen.

Preferred compounds of formula I are also those in which U is $C(R_{15})R_{16}$.

Equally preferred compounds of formula I are those in which R_{15} and R_{16} signify hydrogen.

Equally preferred are compounds of formula I, wherein m is 1, and V is oxygen or sulphur.

Also preferred are compounds of formula I, wherein m is 0.

Further preferred are compounds of formula I, wherein R_1 to R_5 are hydrogen, m is 1, V is oxygen, U is $C(R_{15})R_{16}$ and A is R_7 -Y-.

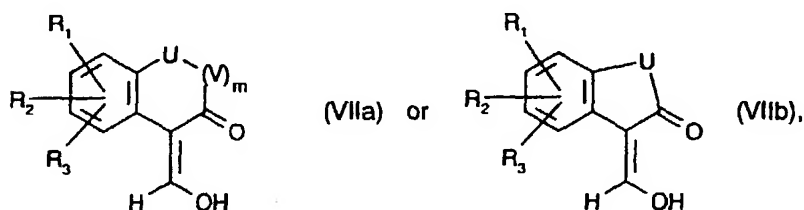
Of these, particular preference is given to those wherein R_{15} and R_{16} signify hydrogen, R_7 is methyl and Y is oxygen.

Important compounds of formula I are those wherein U is $C(R_{15})R_{16}$, m is 0, and R_1 to R_5 and A are defined as under formula I.

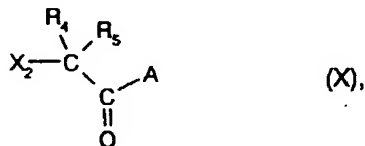
Of these, compounds that are particularly important are those in which R_1 to R_5 , R_{15} and R_{16} are hydrogen, and A is R_7Y .

Of these, the compound in which R_7 is methyl and Y is oxygen is quite particularly important.

The process according to the invention for the production of compounds of formula I takes place analogously to known processes, and is characterised in that a compound of formula VIIa or VIIb



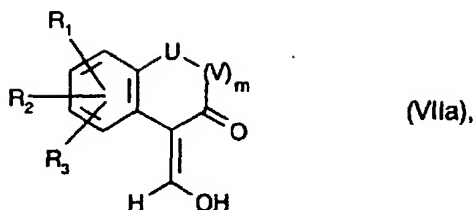
wherein R_1 to R_3 , U, V and m have the significances given under formula I, is allowed to react with a compound of formula X



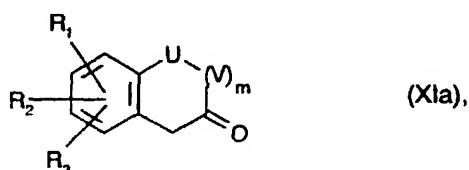
wherein R_4 , R_5 and A have the significances given under formula I, and X_2 signifies a leaving group,

- a) in the presence of a base and an organic solvent at temperatures of 0° to 100°C , or
- b) in the presence of an excess of cesium fluoride in an organic solvent at temperatures of 0° to 50°C .

The process according to the invention for the production of compounds of formula VIIa



wherein R_1 to R_3 , U and V have the significances given under formula I and m is 1, takes place analogously to known processes, and is characterised in that a compound of formula XIa

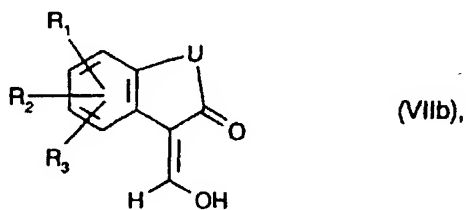


wherein R_1 to R_3 , U , V and m have the significances indicated, is reacted with a compound of formula VIII

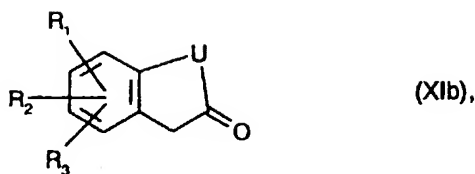


wherein R_0 is C_1 - C_4 -alkyl, in the presence of a base and optionally an organic solvent.

The process according to the invention for the production of compounds of formula VIIb



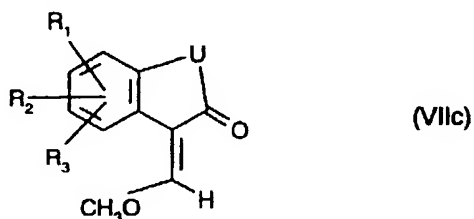
wherein R_1 to R_3 and U have the significances given under formula I, and U is especially oxygen, takes place analogously to known processes, and is characterised in that a compound of formula XIb



wherein R_1 to R_3 and U have the indicated significances, is reacted with a compound of formula IX

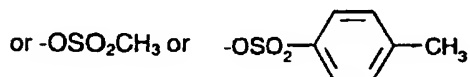


in the presence of an excess of acetic acid anhydride at an elevated temperature for 2 to 24 hours, to form the compound of formula VIIc



and this compound undergoes enol ether cleavage with an aqueous base at 0° to 25°C , and is subsequently worked up under acidic conditions.

For the preparation of the compounds of formula I, e.g. the compounds of formula VIIa or VIIb may be reacted e.g. with an equimolar amount or an excess of reactive compound of formula X, whereby X_2 signifies a leaving group, for example halogen, especially chlorine or bromine,



According to method a), this reaction takes place in an inert organic solvent, such as *N,N*-dimethylformamide (DMF), dichloromethane, tetrahydrofuran, dioxane, benzene, toluene, xylenes, dimethyl sulphoxide (DMSO) or diethylether in the presence of a base at temperatures of 0° to 100°C . Suitable bases are for example sodium or potassium hydride, butyl lithium, alcoholates e.g. sodium methylate, sodium ethylate, sodium *i*-propylate, sodium amylate or sodium *t*-butylate, trialkylamines e.g. triethylamine or tributylamine, *N,N*-dialkylated anilines, sodium amide (NaNH_2), sodium-bis-trimethylsilyl amide ($\text{NaN}(\text{TMS})_2$), potassium-bis-trimethylsilyl amide ($\text{KN}(\text{TMS})_2$) or lithium-bis-trimethylsilyl amide ($\text{LiN}(\text{TMS})_2$).

According to method b), the above reaction is effected e.g. analogously to Synlett 1995, 843, in the presence of an excess (2 equivalents) of cesium fluoride in an inert organic solvent such as N,N-dimethylformamide at temperatures from 0° to 50°C, preferably 0° to 25°C.

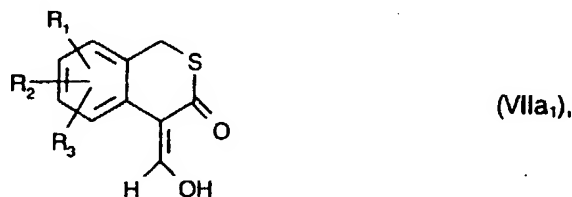
This process b) is especially suitable for reactive and towards bases unstable starting compounds.

The starting compounds of formula VIIa (m=1) and VIIb (m=0) may be produced analogously to known processes, e.g. the former in accordance with the general reaction conditions of a Claisen condensation, as described for example in Houben-Weyl, volume VIII, pages 560-590; ibid, volume VII/2a, pages 492, 495, 535 and 580; and ibid, volume VI/1d, pages 40ff. and page 275, as well as Z. Anal. Chem. 190, 243 (1962).

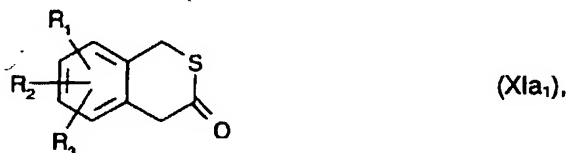
Accordingly, the compound of formula XIa is allowed to react with an ester of formula VIII in the presence of a base and an organic solvent such as benzene, toluene, alcohols such as methanol or ethanol, N,N-dimethylformamide or an ester, whereby the employed ester of formula VIII may itself serve as the solvent. Suitable bases for the above condensation reaction are for example sodium or potassium hydride, alcoholates such as sodium methylate or sodium ethylate, or potassium or sodium metal.

This reaction method is especially suitable for the production of compounds of formula VIIa, wherein m signifies 1.

For example, in the above manner, the new compound of formula VIIa₁



wherein R₁, R₂ and R₃ have the significances given under formula I, may be prepared from the compound of formula XIa₁



wherein R_1 , R_2 and R_3 have the indicated significances.

The compounds of formula VIIa₁ are an important intermediate product for the synthesis of the compounds of formula I. The invention thus also relates to these compounds.

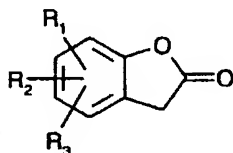
The starting compounds of formula VIIb may be produced e.g. analogously to WO 92/08703, Heterocycles 35, 305 (1993) or Z. Naturforsch. B, 34B, 283 (1979). The compound of formula XIb is accordingly allowed to react with the ortho-ester of formula IX in an excess of acetic acid anhydride (Ac_2O) for 2 to 24 hours at elevated temperatures, e.g. 100°C, to form the enol ether of formula VIIc. This may be cleaved under basic-aqueous conditions at temperatures of 0° to 25°C. Acidic-aqueous working up, for example in the presence of diluted mineral acids such as sulphuric or hydrochloric acid, yields the desired product of formula VIIb.

This method of reaction is especially suitable for the production of compounds of formula VIIb ($m=0$), wherein U has the significance given under formula I with the exception of $C(R_{15})R_{16}$, if R_{15} or R_{16} signifies hydrogen, or R_{15} and R_{16} are hydrogen simultaneously. For these derivatives, special processes are to be considered, e.g. those indicated in Tetrahedron Lett. 32, 851 (1991) or Chem. Ber. 107, 739 (1974).

The starting compounds of formulae VIII, IX, X, XIa and XIb are either known or may be produced according to disclosed processes.

For example, the production of the compound of formula XIa₁ is described in J. Heterocyclic Chem. 20, 811 (1983).

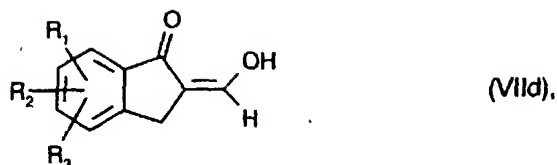
The production of the starting compound of formula XIb₁



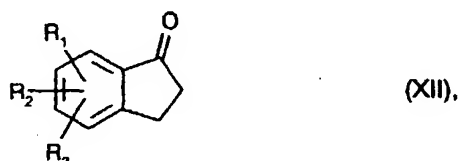
(XIb₁)

wherein R_1 , R_2 and R_3 have the significances given under formula I, is described e.g. in FR-A-2 686 880.

The intermediate products of formula VIId

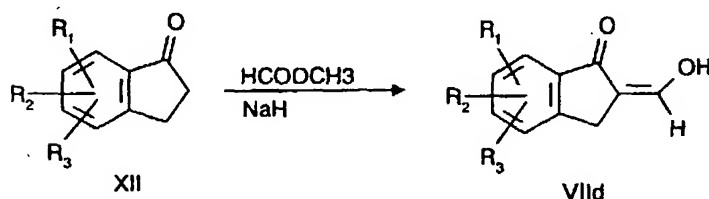


wherein R_1 , R_2 and R_3 have the significances given under formula I, may be produced analogously to known processes, such as that described in J. Chem. Soc. 101, 2546 (1912), from the compounds of formula XII

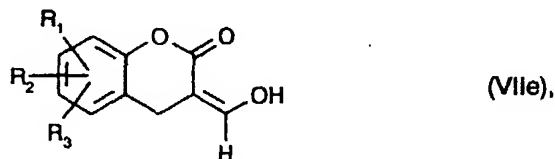


wherein R_1 , R_2 and R_3 have the indicated significances, e.g. in accordance with the following reaction scheme 1.

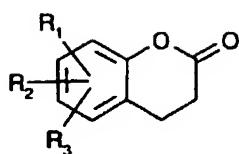
Reaction scheme 1



The intermediate products of formula VIIe



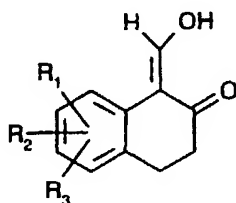
wherein R_1 , R_2 and R_3 have the significances given under formula I, may be produced analogously to known processes, such as that described in Chem. Ber. 93, 1021 (1960), from the compounds of formula XIII



(XIII),

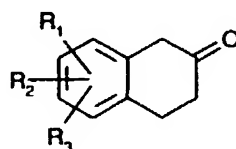
wherein R_1 , R_2 and R_3 have the indicated significances.

The intermediate products of formula VIIf



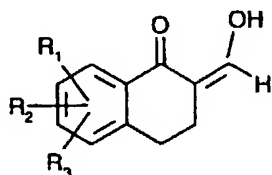
(VIIf),

wherein R_1 , R_2 and R_3 have the significances given under formula I, may be produced analogously to known processes, such as that described in Tetrahedron Lett. 1965, 1599, from the compounds of formula XIa₂

(XIa₂),

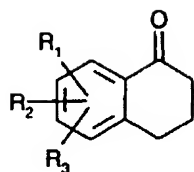
wherein R_1 , R_2 and R_3 have the indicated significances.

The intermediate products of formula VIIg



(VIIg),

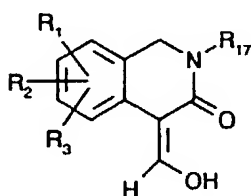
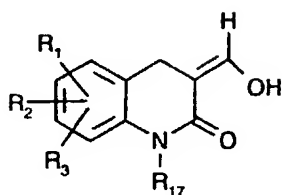
wherein R_1 , R_2 and R_3 have the significances given under formula I, may be produced analogously to known processes, such as that described in J. Org. Chem. 15, 1135 (1950), from the compounds of formula XIVA



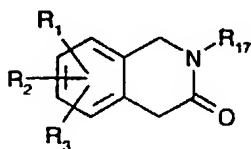
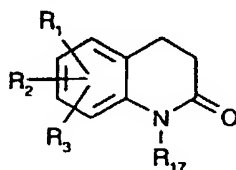
(XIVa).

wherein R_1 , R_2 and R_3 have the indicated significances.

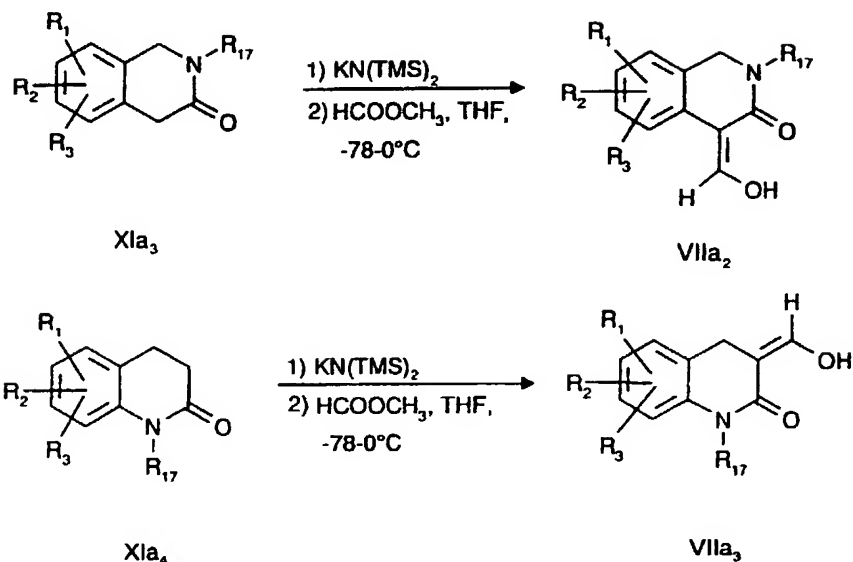
The intermediate products of formulae VIIa₂ and VIIa₃

(VIIa₂) and(VIIa₃).

wherein R_1 , R_2 , R_3 and R_{17} have the significances given under formula I, may be produced from the compounds of formulae XIa₃ or XIa₄

(XIa₃) or(XIa₄).

wherein R_1 , R_2 , R_3 and R_{17} have the indicated significances, e.g. in accordance with the following reaction scheme 2.

Reaction scheme 2

The reaction of the compounds of formulae Xla_3 and Xla_4 with the formic acid ester according to reaction scheme 2 preferably takes place in an organic solvent such as ether, for example tetrahydrofuran (THF), at temperatures of $-78^\circ C$ to $0^\circ C$ and in the presence of a base such as potassium-bis-(trimethylsilyl)-amide ($KN(TMS)_2$).

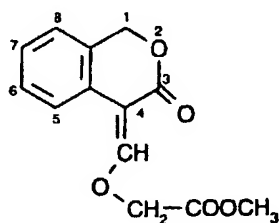
The compounds of formulae $VIIa_2$ and $VIIa_3$ are new and represent important intermediate products in the synthesis of the compounds of formula I. The invention thus also relates to these compounds.

The educts of formula Xla_3 in reaction scheme 2 may be obtained analogously to known processes, e.g. as described in Heterocyclic Chem. 32, 73 (1995).

The educts of formula Xla_4 in reaction scheme 2 may be obtained analogously to known processes, e.g. as described in Synthesis 1987, 515.

The starting compounds of formulae Xla_2 , XII, XIII and XIVa are either known or may be produced according to disclosed processes.

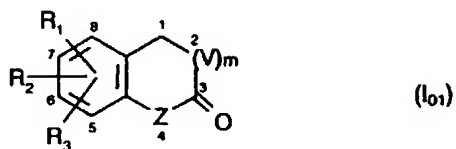
The following example further clarifies the invention without restricting it.

Preparation example H1 : (3-oxo-isochroman-4-ylidenemethoxy)-acetic acid methyl ester

(Comp. No. 01.002)

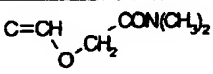
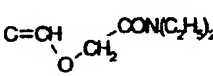
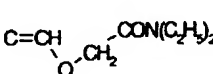
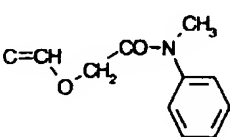
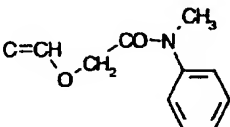
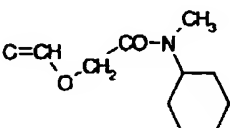
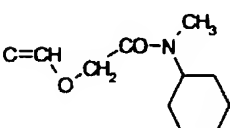
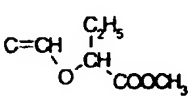
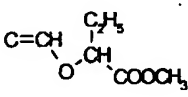
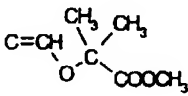
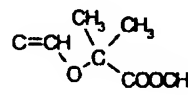
4.48 g (0.025 mols) of 3H-2-benzopyran-3-one-1,4-dihydro-4-hydroxymethylene (Z. Anal. Chem. 190, 243 (1962)) in 10 ml of DMF are added dropwise over the course of 5 minutes at -5°C to a suspension of 1.2 g of sodium hydride (55% in oil) in 120 ml of DMF. Afterwards, 4.0 g (0.026 mols) of bromoacetic acid methyl ester are added. After removing the cooling bath, stirring continues for 1¾ hours at 25°C. The reaction mixture is subsequently poured onto a mixture of 400 ml of ice water / 50 ml of 2N aqueous hydrochloric acid / 200 ml of ethyl acetate, the organic and aqueous phases are separated from one another and washed 3 times each with 100 ml of water and 100 ml of ethyl acetate. The combined organic phases are dried over sodium sulphate and concentrated. The oily residue obtained is triturated with diethylether/hexane and filtered. 5.34 g of the desired product are obtained with a m.p. of 81-82°C.

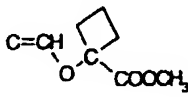
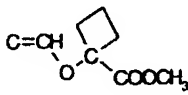
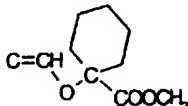
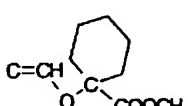
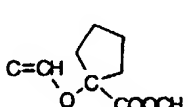
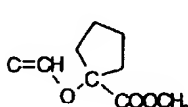
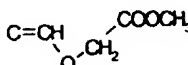
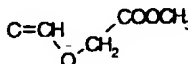
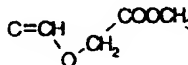
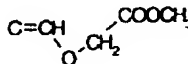
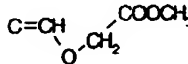
The compounds listed in the following tables may also be produced in analogous manner and according to methods illustrated in the documents cited.

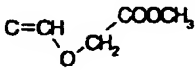
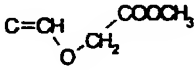
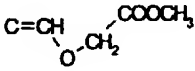
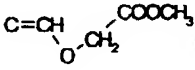
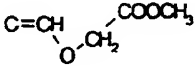
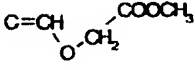
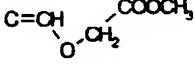
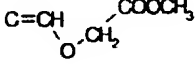
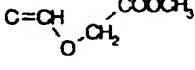
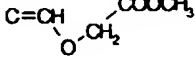
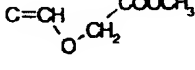
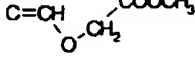
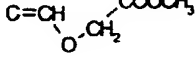
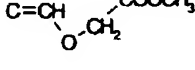
Table 01: Compounds of formula I₀₁

| Comp. No. | R ₁ , R ₂ , R ₃ | Z | V | m | Phys.data |
|-----------|--|---|----------------------|---|-----------|
| | | | | | m.p. [°C] |
| 01.001 | H, H, H | | O | 1 | oil |
| 01.002 | H, H, H | | O | 1 | 81-82 |
| 01.003 | H, H, H | | O | 1 | 83-86 |
| 01.004 | H, H, H | | O | 1 | 44-46 |
| 01.005 | H, H, H | | CH ₂ | 1 | 82-84 |
| 01.006 | H, H, H | | CH ₂ | 1 | 70-72 |
| 01.007 | H, H, H | | S | 1 | 94-95 |
| 01.008 | H, H, H | | S | 1 | 75-76 |
| 01.009 | H, H, H | | NC H ₃ | 1 | solid |

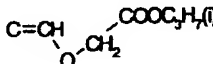
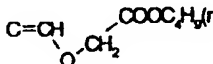
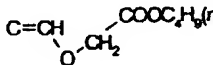
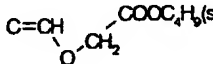
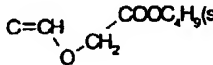
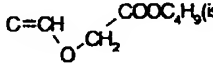
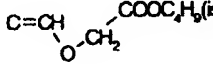
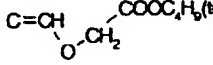
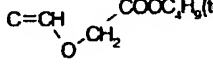
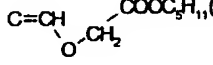
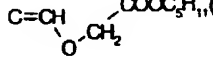
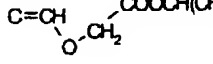
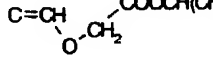
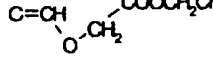
| Comp. No. | R ₁ , R ₂ , R ₃ | Z | V | m | Phys.data |
|-----------|--|---|----------------------|---|-----------|
| | | | | | m.p. [°C] |
| 01.010 | H, H, H | | NC H ₃ | 1 | 126-128 |
| 01.011 | H, H, H | | NC H ₃ | 1 | 134-137 |
| 01.012 | H, H, H | | O | 1 | 104-105 |
| 01.013 | H, H, H | | S | 1 | 128-129 |
| 01.014 | H, H, H | | S | 1 | |
| 01.015 | H, H, H | | O | 1 | |
| 01.016 | H, H, H | | S | 1 | |
| 01.017 | H, H, H | | O | 1 | |
| 01.018 | H, H, H | | S | 1 | |
| 01.019 | H, H, H | | O | 1 | |
| 01.020 | H, H, H | | S | 1 | |
| 01.021 | H, H, H | | O | 1 | |
| 01.022 | H, H, H | | S | 1 | |

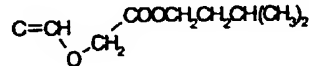
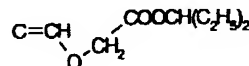
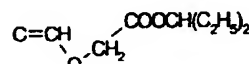
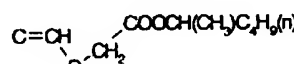
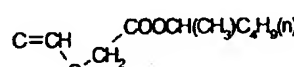
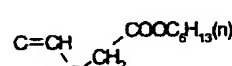
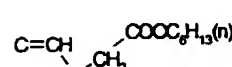
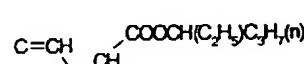
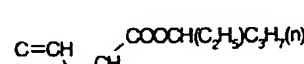
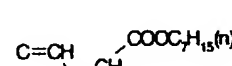
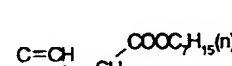
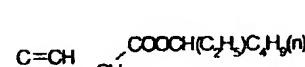
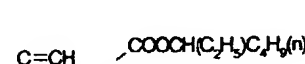
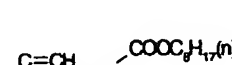
| Comp. No. | R ₁ , R ₂ , R ₃ | Z | V | m | Phys.data |
|-----------|--|---|---|---|-----------|
| | | | | | m.p. [°C] |
| 01.023 | H, H, H |  | O | 1 | |
| 01.024 | H, H, H |  | S | 1 | |
| 01.025 | H, H, H |  | O | 1 | |
| 01.026 | H, H, H |  | S | 1 | |
| 01.027 | H, H, H |  | O | 1 | |
| 01.028 | H, H, H |  | S | 1 | |
| 01.029 | H, H, H |  | O | 1 | |
| 01.030 | H, H, H |  | S | 1 | |
| 01.031 | H, H, H |  | O | 1 | |
| 01.032 | H, H, H |  | S | 1 | |
| 01.033 | H, H, H |  | O | 1 | |

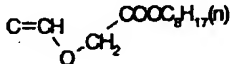
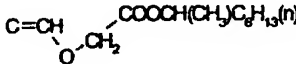
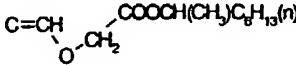
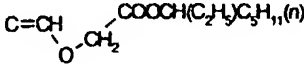
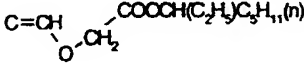
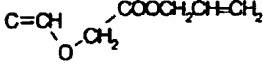
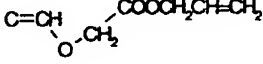
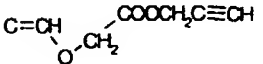
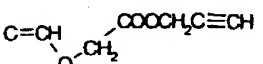
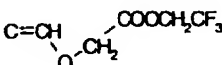
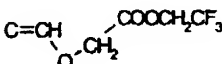
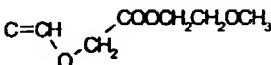
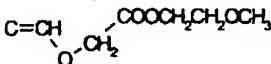
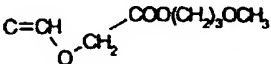
| Comp. No. | R ₁ , R ₂ , R ₃ | Z | V | m | Phys.data |
|-----------|--|---|---|---|-----------|
| | | | | | m.p. [°C] |
| 01.034 | H, H, H |  | S | 1 | |
| 01.035 | H, H, H |  | O | 1 | |
| 01.036 | H, H, H |  | S | 1 | |
| 01.037 | H, H, H |  | O | 1 | |
| 01.038 | H, H, H |  | S | 1 | |
| 01.039 | H, H, H |  | O | 1 | |
| 01.040 | H, 7-CH ₃ , H |  | S | 1 | |
| 01.041 | H, 7-CH ₃ , H |  | O | 1 | |
| 01.042 | H, 6-CH ₃ , H |  | S | 1 | |
| 01.043 | H, 6-CH ₃ , H |  | O | 1 | |
| 01.044 | H, 7-OCH ₃ , H |  | S | 1 | |

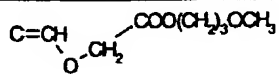
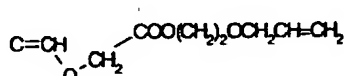
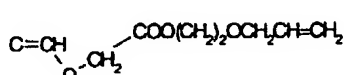
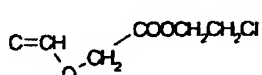
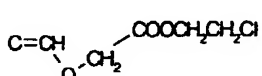
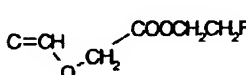
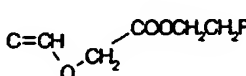
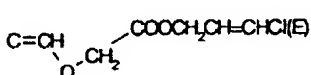
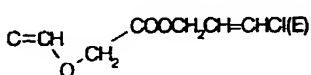
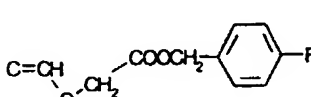
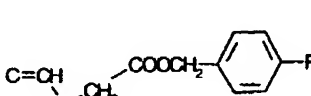
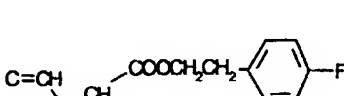
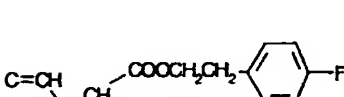
| Comp. No. | R ₁ , R ₂ , R ₃ | Z | V | m | Phys.data |
|--------------|--|---|---|---|-----------|
| | | | | | m.p. [°C] |
| 01.045 | H, 7-OCH ₃ , H |  | O | 1 | |
| 01.046 | H, 7-Cl, H |  | S | 1 | |
| 01.047 | H, 7-Cl, H |  | O | 1 | |
| 01.048 | H, 6-Cl, H |  | S | 1 | |
| 01.049 | H, 6-Cl, H |  | O | 1 | |
| 01.050 | H, 8-CH ₃ , H |  | S | 1 | |
| 01.051 | H, 8-CH ₃ , H |  | O | 1 | |
| 01.052 | H, 5-CH ₃ , H |  | S | 1 | |
| 01.053 | H, 5-CH ₃ , H |  | O | 1 | |
| 01.054 | H, 8-Cl, H |  | S | 1 | |
| 01.055 | H, 8-Cl, H |  | O | 1 | |
| 01.056 | H, 5-Cl, H |  | S | 1 | |
| 01.057 | H, 5-Cl, H |  | O | 1 | |
| 01.058 | H, 6-OCH ₃ , H |  | S | 1 | |

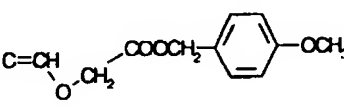
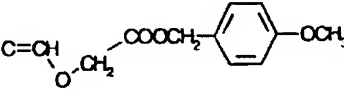
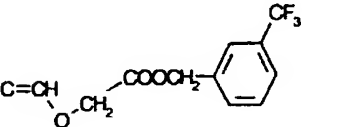
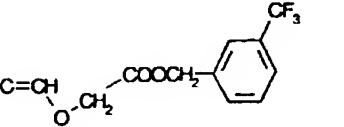
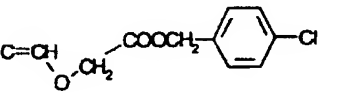
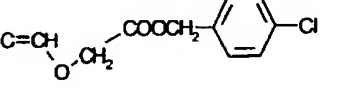
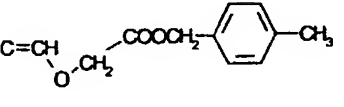
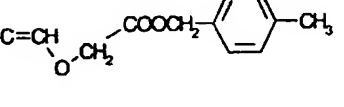
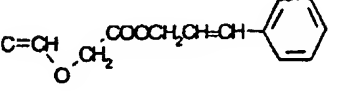
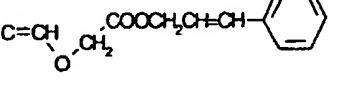
| Comp. No. | R ₁ , R ₂ , R ₃ | Z | V | m | Phys.data |
|--------------|--|---|----|---|-----------|
| | | | | | m.p. [°C] |
| 01.059 | H, 6-OCH ₃ , H | | O | 1 | |
| 01.060 | H, 8-OCH ₃ , H | | S | 1 | |
| 01.061 | H, 8-OCH ₃ , H | | O | 1 | |
| 01.062 | H, 5-OCH ₃ , H | | S | 1 | |
| 01.063 | H, 5-OCH ₃ , H | | O | 1 | |
| 01.064 | 6-OCH ₃ , 7-OCH ₃ , H | | S | 1 | |
| 01.065 | 6-OCH ₃ , 7-OCH ₃ , H | | O | 1 | |
| 01.066 | 6-CH ₃ , 7-CH ₃ , H | | S | 1 | |
| 01.067 | 6-CH ₃ , 7-CH ₃ , H | | O | 1 | |
| 01.068 | H, H, H | | NH | 1 | |
| 01.069 | H, H, H | | NH | 1 | |
| 01.070 | H, H, H | | O | 1 | |
| 01.071 | H, H, H | | S | 1 | |
| 01.072 | H, H, H | | O | 1 | |

| Comp. No. | R ₁ , R ₂ , R ₃ | Z | V | m | Phys.data |
|--------------|--|---|---|---|-----------|
| | | | | | m.p. [°C] |
| 01.073 | H, H, H |  | S | 1 | |
| 01.074 | H, H, H |  | O | 1 | |
| 01.075 | H, H, H |  | S | 1 | |
| 01.076 | H, H, H |  | O | 1 | |
| 01.077 | H, H, H |  | S | 1 | |
| 01.078 | H, H, H |  | O | 1 | |
| 01.079 | H, H, H |  | S | 1 | |
| 01.080 | H, H, H |  | O | 1 | |
| 01.081 | H, H, H |  | S | 1 | |
| 01.082 | H, H, H |  | O | 1 | |
| 01.083 | H, H, H |  | S | 1 | |
| 01.084 | H, H, H |  | O | 1 | |
| 01.085 | H, H, H |  | S | 1 | |
| 01.086 | H, H, H |  | O | 1 | |

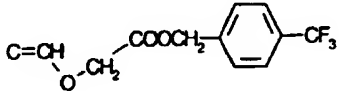
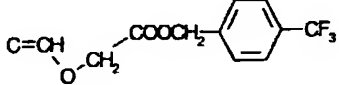
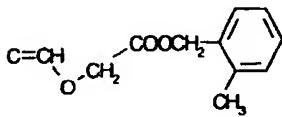
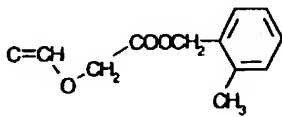
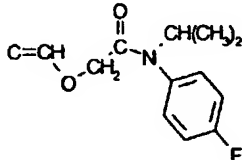
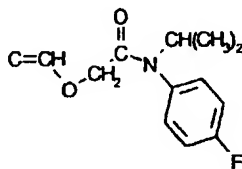
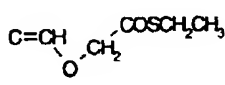
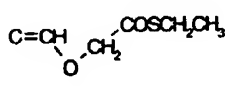
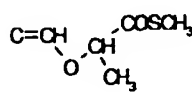
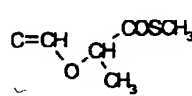
| Comp. No. | R ₁ , R ₂ , R ₃ | Z | V | m | Phys.data m.p. [°C] |
|--------------|--|---|---|---|----------------------------|
| 01.087 | H, H, H |  | S | 1 | |
| 01.088 | H, H, H |  | O | 1 | |
| 01.089 | H, H, H |  | S | 1 | |
| 01.090 | H, H, H |  | O | 1 | |
| 01.091 | H, H, H |  | S | 1 | |
| 01.092 | H, H, H |  | O | 1 | |
| 01.093 | H, H, H |  | S | 1 | |
| 01.094 | H, H, H |  | O | 1 | |
| 01.095 | H, H, H |  | S | 1 | |
| 01.096 | H, H, H |  | O | 1 | |
| 01.097 | H, H, H |  | S | 1 | |
| 01.098 | H, H, H |  | O | 1 | |
| 01.099 | H, H, H |  | S | 1 | |
| 01.100 | H, H, H |  | O | 1 | |

| Comp. No. | R ₁ , R ₂ , R ₃ | Z | V | m | Phys.data |
|--------------|--|---|---|---|-----------|
| | | | | | m.p. [°C] |
| 01.101 | H, H, H |  | S | 1 | |
| 01.102 | H, H, H |  | O | 1 | |
| 01.103 | H, H, H |  | S | 1 | |
| 01.104 | H, H, H |  | O | 1 | |
| 01.105 | H, H, H |  | S | 1 | |
| 01.106 | H, H, H |  | O | 1 | |
| 01.107 | H, H, H |  | S | 1 | |
| 01.108 | H, H, H |  | O | 1 | |
| 01.109 | H, H, H |  | S | 1 | |
| 01.110 | H, H, H |  | O | 1 | |
| 01.111 | H, H, H |  | S | 1 | |
| 01.112 | H, H, H |  | O | 1 | |
| 01.113 | H, H, H |  | S | 1 | |
| 01.114 | H, H, H |  | O | 1 | |

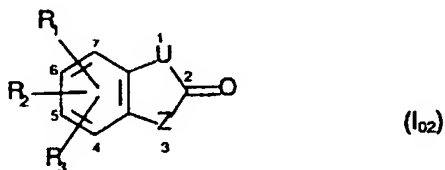
| Comp. No. | R ₁ , R ₂ , R ₃ | Z | V | m | Phys.data |
|-----------|--|---|---|---|-----------|
| | | | | | m.p. [°C] |
| 01.115 | H, H, H |  | S | 1 | |
| 01.116 | H, H, H |  | O | 1 | |
| 01.117 | H, H, H |  | S | 1 | |
| 01.118 | H, H, H |  | O | 1 | |
| 01.119 | H, H, H |  | S | 1 | |
| 01.120 | H, H, H |  | O | 1 | |
| 01.121 | H, H, H |  | S | 1 | |
| 01.122 | H, H, H |  | O | 1 | |
| 01.123 | H, H, H |  | S | 1 | |
| 01.124 | H, H, H |  | O | 1 | |
| 01.125 | H, H, H |  | S | 1 | |
| 01.126 | H, H, H |  | O | 1 | |
| 01.127 | H, H, H |  | S | 1 | |

| Comp. No. | R ₁ , R ₂ , R ₃ | Z | V | m | Phys.data |
|-----------|--|---|---|---|-----------|
| | | | | | m.p. [°C] |
| 01.128 | H, H, H |  | O | 1 | |
| 01.129 | H, H, H |  | S | 1 | |
| 01.130 | H, H, H |  | O | 1 | |
| 01.131 | H, H, H |  | S | 1 | |
| 01.132 | H, H, H |  | O | 1 | |
| 01.133 | H, H, H |  | S | 1 | |
| 01.134 | H, H, H |  | O | 1 | |
| 01.135 | H, H, H |  | S | 1 | |
| 01.136 | H, H, H |  | O | 1 | |
| 01.137 | H, H, H |  | S | 1 | |

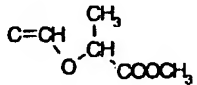
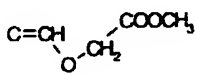
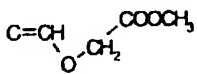
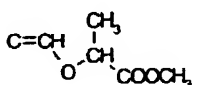
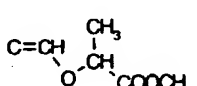
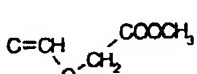
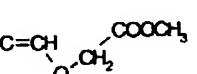
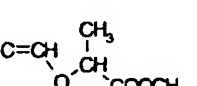
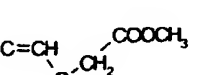
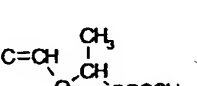
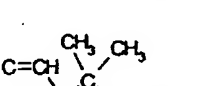
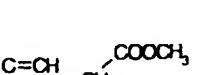
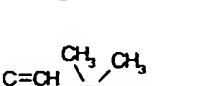
| Comp. No. | R ₁ , R ₂ , R ₃ | Z | V | m | Phys.data |
|-----------|--|---|---|---|-----------|
| | | | | | m.p. [°C] |
| 01.138 | H, H, H | | O | 1 | |
| 01.139 | H, H, H | | S | 1 | |
| 01.140 | H, H, H | | O | 1 | |
| 01.141 | H, H, H | | S | 1 | |
| 01.142 | H, H, H | | O | 1 | |
| 01.143 | H, H, H | | S | 1 | |
| 01.144 | H, H, H | | O | 1 | |
| 01.145 | H, H, H | | S | 1 | |
| 01.146 | H, H, H | | O | 1 | |
| 01.147 | H, H, H | | S | 1 | |
| 01.148 | H, H, H | | O | 1 | |
| 01.149 | H, H, H | | S | 1 | |

| Comp. No. | R ₁ , R ₂ , R ₃ | Z | V | m | Phys.data |
|-----------|--|---|---|---|-----------|
| | | | | | m.p. [°C] |
| 01.150 | H, H, H |  | O | 1 | |
| 01.151 | H, H, H |  | S | 1 | |
| 01.152 | H, H, H |  | O | 1 | |
| 01.153 | H, H, H |  | S | 1 | |
| 01.154 | H, H, H |  | O | 1 | |
| 01.155 | H, H, H |  | S | 1 | |
| 01.156 | H, H, H |  | O | 1 | |
| 01.157 | H, H, H |  | S | 1 | |
| 01.158 | H, H, H |  | O | 1 | |
| 01.159 | H, H, H |  | S | 1 | |

| Comp. No. | R ₁ , R ₂ , R ₃ | Z | V | m | Phys.data m.p. [°C] |
|-----------|--|---|---|---|------------------------|
| 01.160 | H, H, H | | O | 1 | |
| 01.161 | H, H, H | | S | 1 | |

Table 02: Compounds of formula I₀₂

| Comp. No. | U | R ₁ , R ₂ , R ₃ | Z | Phys. data m.p. [°C] |
|-----------|-----------------|--|---|-------------------------|
| 02.001 | O | H, H, H | | 114-117 |
| 02.002 | O | H, H, H | | 108-117 |
| 02.003 | O | H, 5-Cl, H | | 148-150 |
| 02.004 | CH ₂ | H, H, H | | 113-117 |
| 02.005 | CH ₂ | H, H, H | | 114-116 |
| 02.006 | CH ₂ | H, H, H | | 83-85 |

| Comp. No. | U | R ₁ , R ₂ , R ₃ | Z | Phys. data m.p. [°C] |
|-----------|------------------|--|---|-------------------------|
| 02.007 | NH | H, 5-Cl, H |  | 196-197 |
| 02.008 | NH | H, 5-Cl, H |  | 157-159 |
| 02.009 | NH | H, H, H |  | 169-171 |
| 02.010 | NH | H, H, H |  | resin |
| 02.011 | NCH ₃ | H, H, H |  | 146-147 |
| 02.012 | NCH ₃ | H, H, H |  | 111-112 |
| 02.013 | S | H, H, H |  | |
| 02.014 | S | H, H, H |  | |
| 02.015 | CH ₂ | H, 6-Cl, H |  | |
| 02.016 | CH ₂ | H, 6-Cl, H |  | |
| 02.017 | CH ₂ | H, 6-Cl, H |  | |
| 02.018 | CH ₂ | H, 6-OCH ₃ , H |  | |
| 02.019 | CH ₂ | H, 6-OCH ₃ , H |  | |

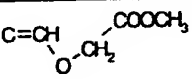
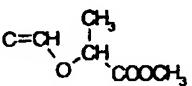
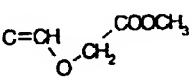
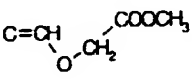
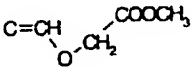
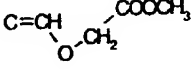
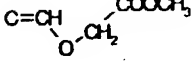
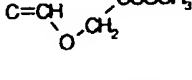
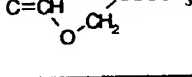
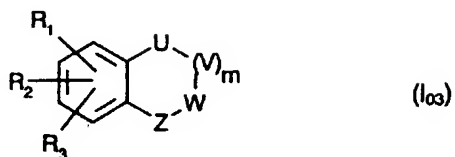
| Comp. No. | U | R ₁ , R ₂ , R ₃ | Z | Phys. data m.p. [°C] |
|-----------|-----------------|--|---|-------------------------|
| 02.020 | CH ₂ | 6-CH ₃ , H, H |  | |
| 02.021 | CH ₂ | 6-CH ₃ , H, H |  | |
| 02.022 | CH ₂ | H, 5-Cl, H |  | |
| 02.023 | CH ₂ | 5-OCH ₃ , H, H |  | |
| 02.024 | CH ₂ | 5-CH ₃ , H, H |  | |
| 02.025 | CH ₂ | 5-OCH ₃ , 6-OCH ₃ , H |  | |
| 02.026 | CH ₂ | 5-CH ₃ , 6-CH ₃ , H |  | |
| 02.027 | CH ₂ | 7-CH ₃ , H, H |  | |
| 02.028 | CH ₂ | 4-CH ₃ , H, H |  | |

Table 03: Compounds of formula I₀₃

| Comp. No. | U | V | m | W | Z | R ₁ , R ₂ , R ₃ | Phys. data m.p. [°C] |
|-----------|------------------|-----------------|---|---|-----------------|--|-------------------------|
| 03.001 | O | C=O | 1 | | CH ₂ | H, H, H | waxy |
| 03.002 | O | C=O | 1 | | CH ₂ | H, H, H | 71-73 |
| 03.003 | CH ₂ | C=O | 1 | | CH ₂ | H, H, H | 123-125 |
| 03.004 | CH ₂ | C=O | 1 | | CH ₂ | H, H, H | 98-100 |
| 03.005 | CH ₂ | CH ₂ | 1 | | C=O | H, H, H | 97-98 |
| 03.006 | CH ₂ | CH ₂ | 1 | | C=O | H, H, H | 55-58 |
| 03.007 | NCH ₃ | C=O | 1 | | CH ₂ | H, H, H | waxy |

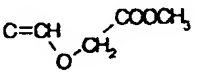
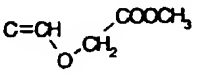
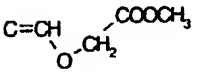
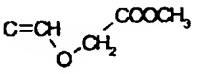
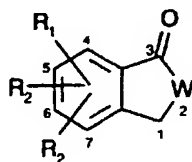
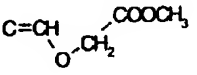
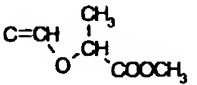
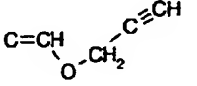
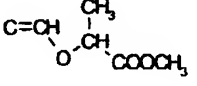
| Comp. No. | U | V | m | W | Z | R ₁ , R ₂ , R ₃ | Phys. data m.p. [°C] |
|-----------|----------------------------------|---|---|-----|---|--|-------------------------|
| 03.008 | CHCH ₃ | O | 1 | C=O |  | H, H, H | |
| 03.009 | CHCH ₃ | S | 1 | C=O |  | H, H, H | |
| 03.010 | C(CH ₃) ₂ | O | 1 | C=O |  | H, H, H | |
| 03.011 | C(CH ₃) ₂ | S | 1 | C=O |  | H, H, H | |

Table 04: Compounds of formula I₀₄(I₀₄)

| Comp. No. | R ₁ , R ₂ , R ₃ | W | Phys. data m.p. [°C] |
|-----------|--|---|-------------------------|
| 04.001 | H, 6-Cl, H |  | 144-146 |
| 04.002 | H, 6-Cl, H |  | 98-100 |
| 04.003 | H, H, H |  | 119-121 |
| 04.004 | H, H, H |  | 104-106 |

| Comp. No. | R ₁ , R ₂ , R ₃ | W | Phys. data m.p. [°C] |
|-----------|--|------------------------------|-------------------------|
| 04.005 | H, H, H | <chem>C=CC(OC)C(=O)OC</chem> | 114-116 |

The compounds of formula I according to the invention may be used as antidotes in herbicidal compositions.

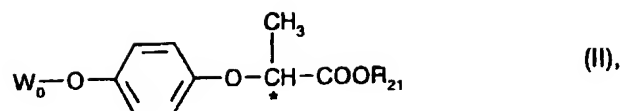
When using herbicides, the cultivated plants may also be damaged to a considerable extent e.g. depending on the dosage of herbicide and the type of application, the plant being cultivated, the constitution of the soil and the climatic conditions, such as duration of light, temperature and amount of rainfall.

In order to counteract this and similar problems, already many substances have been proposed as antidotes. These are capable of antagonizing the damaging activity of the herbicide on the cultivated plant, that is, protecting the cultivated plant therefrom, whereby however the herbicide activity on the weeds to be controlled is practically unimpaired. As a result, it has been shown that the proposed antidotes often have very specific activity both in regard of the cultivated plants and in regard of the herbicide and partly also depending on the type of application. This means that a certain antidote is often only suitable for a certain cultivated plant and a particular class of herbicide substance or a certain herbicide.

It has now been found that the compounds of formula I according to the invention are suitable for protecting cultivated plants from the phytotoxic activity of certain classes of aryloxy-phenoxypropionic acid ester, sulphonylurea, sulphonamide, 3-hydroxy-4-aryl-5-oxo-pyrazoline and chloracetanilide herbicides and the herbicide isoxaflutol (EXP-30953).

Thus, in accordance with the invention, a herbicidal composition having selective herbicide activity is also proposed, which is characterised in that, in addition to the usual inert formulation assistants such as carriers, solvents and wetting agents, it contains as the active ingredient a mixture of

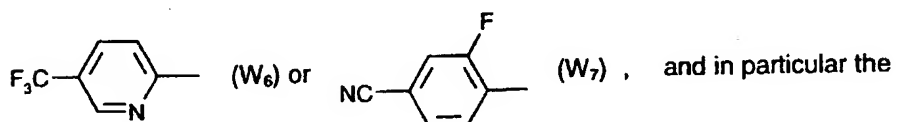
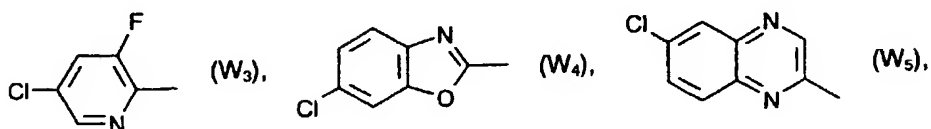
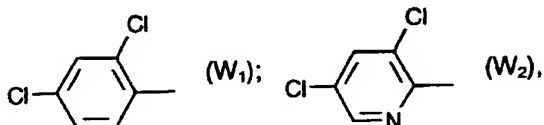
- a) a herbicidally active amount of a herbicide of formulae II to VII



wherein

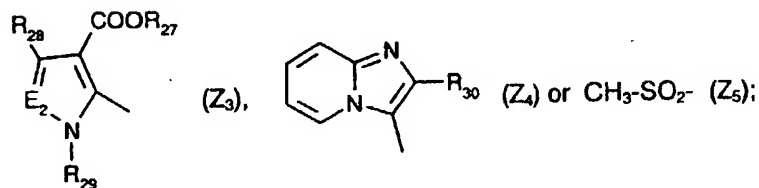
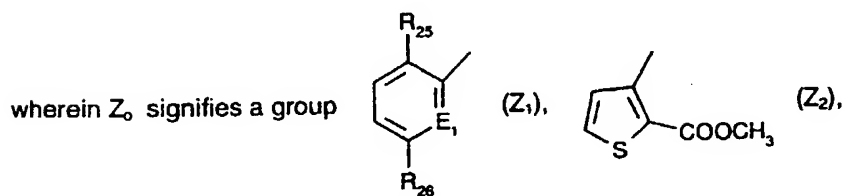
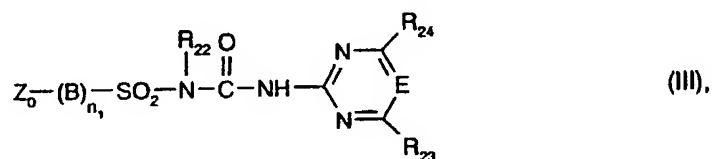
R_{21} signifies C_1 - C_4 -alkyl, propargyl or the group $-\text{CH}_2-\text{CH}_2-\text{O}-\text{N}=\text{C}(\text{CH}_3)_2$; and

W_0 signifies the groups



(R)-enantiomers (*) of these compounds; or


of formula III




R₂₂ signifies hydrogen or CH₃;

R₂₃ signifies CH₃, -OCH₃, -OCHF₂, Cl, -N(CH₃)₂, -NHCH₃ or CF₃;

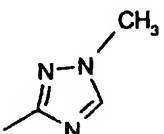
R₂₄ signifies CH₃, -OCH₃, -OCHF₂, -OCH₂CF₃ or -OC₂H₅;

R₂₅ signifies -OC₂H₅, -OCH₂CH₂Cl, -COOCH₃, -COOC₂H₅, -COO-O .

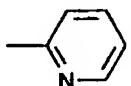
-O-CH₂CH₂-O-CH₃, Cl, -CON(CH₃)₂, -SO₂C₂H₅, CF₃, -OCHF₂, -CO- , -N(CH₃)SO₂CH₃ or

-N(CH₃)COCH₃;

R₂₆ signifies hydrogen, CH₃, -OCH₃, CF₃, CHF₂ or -OCHF₂;

R₂₇ signifies CH₃, C₂H₅ or the group  ;

R₂₈ signifies hydrogen or chlorine;

R₂₉ signifies CH₃ or the group  ;

R₃₀ signifies -SO₂C₂H₅ or chlorine;

E signifies nitrogen or methine;

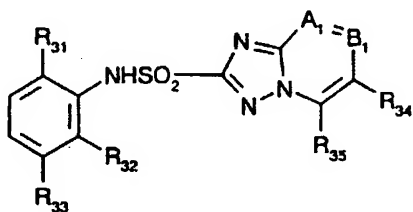
E₁ signifies nitrogen, methine or C-CH₃;

E₂ signifies nitrogen or methine;

B signifies oxygen, -NH- or methylene; and

n₁ signifies 0 or 1,

as well as agronomically compatible salts of these compounds; or
of formula IV



(IV),

wherein

R₃₁ is fluorine or chlorine;

R₃₂ is fluorine, chlorine or -COOCH₃;

R₃₃ is hydrogen or methyl;

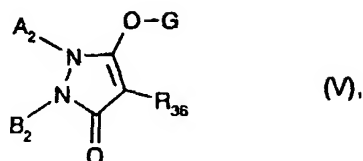
R₃₄ is hydrogen or fluorine;

R_{35} is hydrogen or methoxy;

A_1 is nitrogen or $C-OC_2H_5$; and

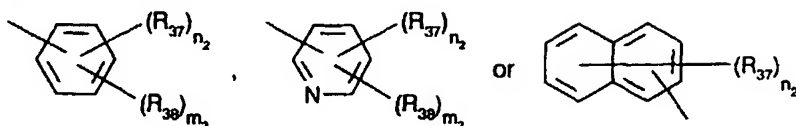
B_1 is nitrogen, $C-CH_3$ or $C-OCH_3$; or

of formula V



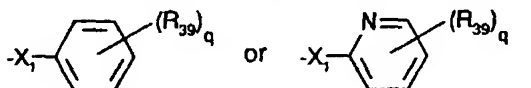
wherein

R_{36} signifies the group



the substituents R_{37} , independently of one another, signify halogen, nitro, cyano, C_1-C_4 -alkyl, C_1-C_4 -halogen-alkyl, C_1-C_{10} -alkoxy, C_1-C_4 -halogen-alkoxy, C_3-C_6 -alkenyloxy, C_1-C_4 -alkoxy- C_2-C_4 -alkoxy, C_3-C_6 -alkinyloxy, C_1-C_4 -alkylcarbonyl, C_1-C_4 -alkoxycarbonyl, C_1-C_4 -alkylthio, C_1-C_4 -alkylsulphanyl, C_1-C_4 -alkylsulphonyl, amino, C_1-C_4 -alkylamino or di- C_1-C_4 -alkylamino;

R_{38} signifies the group



n_2 signifies 0, 1, 2, 3 or 4;

m_2 signifies 0 or 1, whereby the sum of m_2 and n_2 is 0, 1, 2, 3 or 4;

q signifies 0, 1, 2 or 3;

X_1 is oxygen, sulphur, $-CH_2-$ or $-N(R_{40})-$;

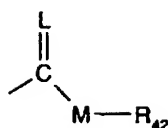
the substituents R_{39} , independently of one another, are C_1-C_4 -alkyl, halogen, C_1-C_4 -halogen-alkyl, C_1-C_4 -alkoxy, C_1-C_4 -halogen-alkoxy, nitro, cyano, C_1-C_4 -alkoxycarbonyl, amino, C_1-C_4 -alkylamino or di- C_1-C_4 -alkylamino;

R_{40} signifies hydrogen, C_1-C_4 -alkyl, formyl or C_1-C_4 -alkylcarbonyl;

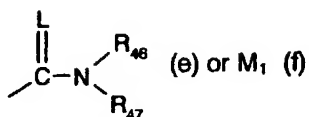
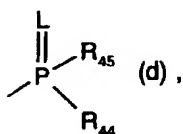
A_2 and B_2 , independently of one another, signify hydrogen, alkyl, alkenyl, alkynyl, alkoxyalkyl, alkylthioalkyl or cycloalkyl, or optionally substituted aryl; or

A_2 and B_2 together form the bivalent radical of a saturated or unsaturated and optionally substituted mono-, bi-, tri- or polycyclic system;

G signifies hydrogen or the groups $-\text{CO}-\text{R}_{41}$ (a),



(b), $-\text{SO}_2-\text{R}_{43}$ (c),



L and M, independently of one another, are oxygen or sulphur;

R_{41} is halogen-alkyl, alkenyl, alkoxyalkyl, alkylthioalkyl, polyalkoxyalkyl or cycloalkyl, which may contain hetero atoms, optionally substituted phenyl, optionally substituted phenylalkyl, substituted heteroaryl, substituted phenoxyalkyl or substituted heteroaryloxyalkyl;

R_{42} is halogen-alkyl, alkenyl, alkoxyalkyl or polyalkoxyalkyl, or optionally substituted phenyl or benzyl;

R_{43} , R_{44} and R_{45} , independently of one another, are alkyl, halogen-alkyl, alkoxy, alkylamino, dialkylamino, alkylthio, alkenylthio, alkynylthio or cycloalkylthio, or optionally substituted phenyl, phenoxy or phenylthio;

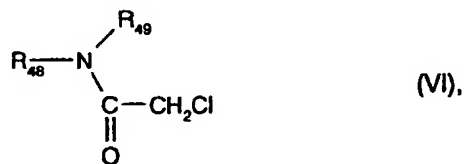
R_{46} and R_{47} , independently of one another, are hydrogen, alkyl, halogen-alkyl, alkenyl, alkoxy or alkoxyalkyl, optionally substituted phenyl or benzyl; or

R_{46} and R_{47} together form an alkylene radical, which may optionally contain oxygen as a hetero atom; and

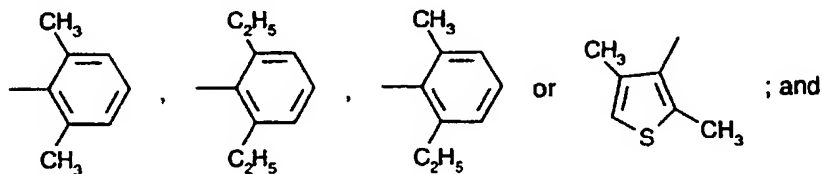
M_1 signifies a metal ion equivalent or an ammonium ion,

as well as salts and diastereoisomers of the compounds of formula V; or

of formula VI

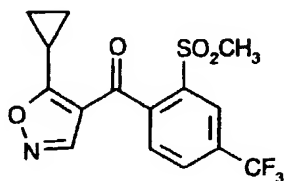


wherein R_{48} signifies a group



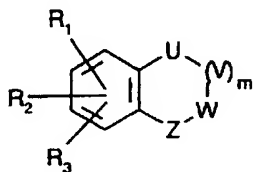
R₄₉ signifies a group -CH(CH₃)CH₂OCH₃, -CH₂OCH₃ or -CH₂OC₂H₅; or

of formula VII



(VII, Isoxaflutol EXP-30953); and

b) an amount of an antidote of formula I



(I),

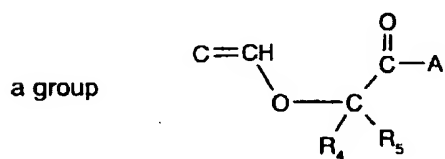
having herbicide-antagonistic activity, wherein

R₁ is hydrogen, C₁-C₄-alkyl, C₁-C₄-alkyl substituted by C₁-C₄-alkyl-X- or C₁-C₄-halogen-alkyl-X-, C₁-C₄-halogen-alkyl, nitro, cyano, -COOR₈, -NR₉R₁₀, -SO₂NR₁₁R₁₂ or -CONR₁₃R₁₄;

R₂ is hydrogen, halogen, C₁-C₄-alkyl, trifluoromethyl, C₁-C₄-alkoxy or C₁-C₄-halogen-alkoxy;

R₃ is hydrogen, halogen or C₁-C₄-Alkyl;

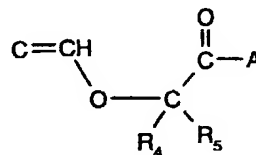
U, V, W and Z independently of one another, are oxygen, sulphur, C(R₁₅)R₁₆, carbonyl, NR₁₇ or



with the provisos that

a) at least one of the ring members U, V, W or Z is carbonyl, and a ring member which is

adjacent to this or these ring members signifies the group



whereby this group only appears once; and

b) two adjacent ring members U and V, V and W and W and Z may not simultaneously signify oxygen;

R₄ and R₅, independently of one another, signify hydrogen or C₁-C₈-alkyl; or

R₄ and R₅ together form a C₂-C₆-alkylene group;

A is R₇-Y- or -NR₁₈R₁₉;

X is oxygen or -S(O)_p;

Y is oxygen or sulphur;

R₇ is hydrogen, C₁-C₈-alkyl, C₁-C₈-halogen-alkyl, C₁-C₄-alkoxy-C₁-C₈-alkyl, C₃-C₆-alkenyloxy-C₁-C₈-alkyl or phenyl-C₁-C₈-alkyl, whereby the phenyl ring may be substituted by halogen, C₁-C₄-alkyl, trifluoromethyl, methoxy or methyl-S(O)_p-; C₃-C₆-alkenyl, C₃-C₆-halogen-alkenyl, phenyl-C₃-C₆-alkenyl, C₃-C₆-alkinyl, phenyl-C₃-C₆-alkinyl, oxetanyl, furfuryl or tetrahydrofurfuryl;

R₈ is hydrogen or C₁-C₄-alkyl;

R₉ is hydrogen, C₁-C₄-alkyl or C₁-C₄-alkylcarbonyl;

R₁₀ is hydrogen or C₁-C₄-alkyl; or

R₉ and R₁₀ together form a C₄- or C₅-alkylene group;

R₁₁, R₁₂, R₁₃ and R₁₄ independently of one another, are hydrogen or C₁-C₄-alkyl; or R₁₁ together with R₁₂ or R₁₃ together with R₁₄ independently of one another, are C₄- or C₅-alkylene, whereby one carbon atom may be replaced by oxygen or sulphur, or one or two carbon atoms may be replaced by -NR₁₅-;

R₁₅ and R₁₆ independently of one another, are hydrogen or C₁-C₈-alkyl; or

R₁₅ and R₁₆ together are C₂-C₆-alkylene;

R₁₇ is hydrogen, C₁-C₈-alkyl, optionally substituted phenyl or benzyl optionally substituted on the phenyl ring;

R₁₈ is hydrogen, C₁-C₈-alkyl, phenyl, phenyl-C₁-C₈-alkyl, whereby the phenyl ring may be substituted by fluorine, chlorine, bromine, nitro, cyano, -OCH₃, C₁-C₄-alkyl or CH₃SO₂-; C₁-C₄-alkoxy-C₁-C₈-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkinyl or C₃-C₆-cycloalkyl;

R₁₉ is hydrogen, C₁-C₈-alkyl, C₃-C₆-alkenyl or C₃-C₆-alkinyl; or

R₁₈ and R₁₉ together are C₄- or C₅-alkylene, whereby one carbon atom may be replaced by oxygen or sulphur, or one or two carbon atoms may be replaced by -NR₂₀-;

R₂₀ is hydrogen or C₁-C₄-alkyl;

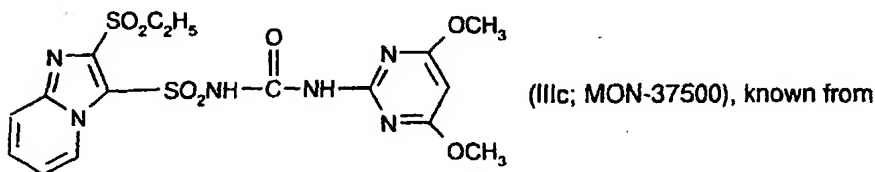
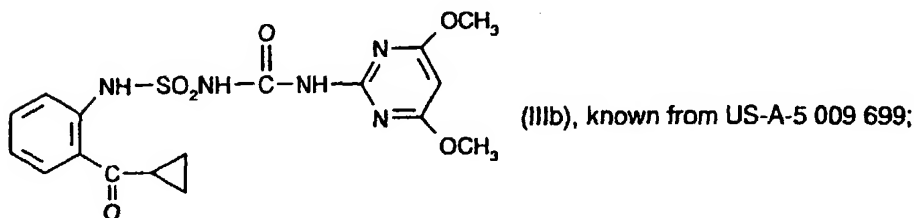
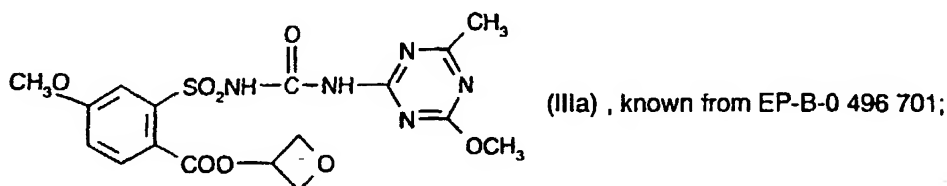
m is 0 or 1; and

p signifies 0, 1 or 2,

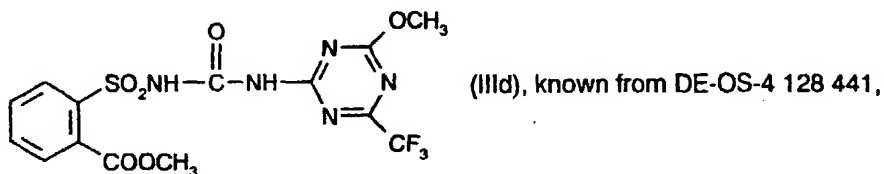
as well as agronomically compatible salts and stereoisomers of these compounds.

Preferred compositions according to the present invention contain clodinafop, quizalafop, propaquizafop, fenoxaprop, fluazifop and cyhalofop as the herbicides of formula II.

Preferred compositions according to the present invention contain tribenuron, metsulfuron, primisulfuron, ethametsulfuron, sulfometuron, chlorimuron, oxasulfuron [presented on the occasion of the Brighton Crop Protection Conference - Weeds - 1995 (Plenary Session 2, November 21, 1995, Proceedings Vol. 2, page 79)], triasulfuron, cinosulfuron, triflusulfuron, bensulfuron, ethoxysulfuron, sulfazuron, nicosulfuron, rimsulfuron, flupyrsulfuron, thifensulfuron, clopyrazosulfuron (NC-319), pyrazosulfuron (NC-311), sulfosulfuron (NC-330, known from US-A-4 895 590), azimsulfuron and amidosulfuron as the herbicides of formula III, as well as the compounds of formulae IIIa to IIId

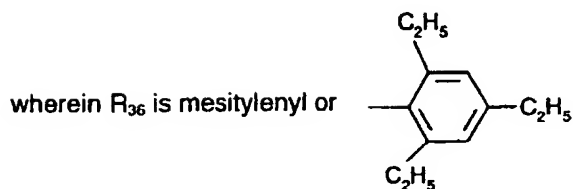
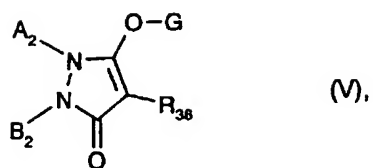


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Preferred compositions according to the present invention contain flumetsulam, metosulam and cloransulam as herbicides of formula IV.

Preferred compositions according to the present invention contain the herbicides of formula V

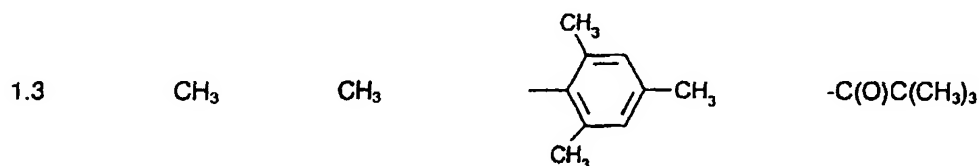


A_2 and B_2 are methyl; or A_2 and B_2 together form a $-(CH_2)_4-$ group; and G signifies hydrogen or $-COC(CH_3)_3$.

Of these, the herbicides of formula V according to table 1 are preferred in particular.

Table 1: Especially preferred herbicides of formula V

| Comp. No. | A_2 | B_2 | R_{36} | G |
|-----------|--------------|-------|----------|-----|
| 1.1 | $-(CH_2)_4-$ | | | H |
| 1.2 | $-(CH_2)_4-$ | | | H |

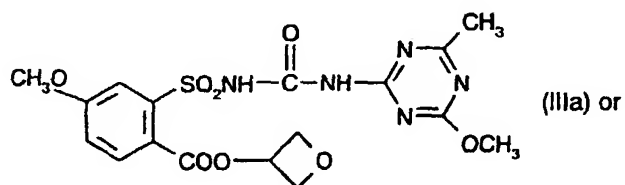


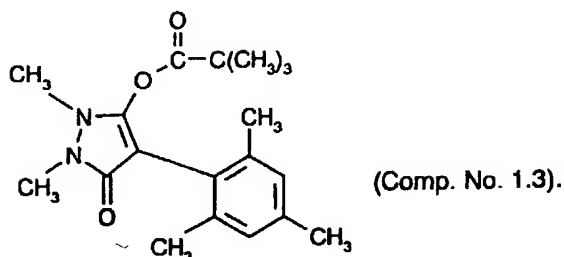
Preferred compositions according to the present invention contain metolachlor, alachlor, acetochlor, dimethenamide and in particular aRS,1'S(-)N-(1'-methyl-2'-methoxyethyl)-N-chloracetyl-2-ethyl-6-methylaniline, known from US-A-5 002 606, as herbicides of formula VI.

The compounds described by common names e.g. under formula II, such as clodinafop, under formula III such as primisulfuron, under formula IV such as flumetsulam, under formula VI such as metolachlor and under formula VII (isoxaflutol) are known in part as commercial products or may be referred to for example in current agrochemical handbooks, e.g. 'The Pesticide Manual', The British Crop Protection Council, London; or 'The Agrochemicals Handbook', The Royal Society of Chemistry.

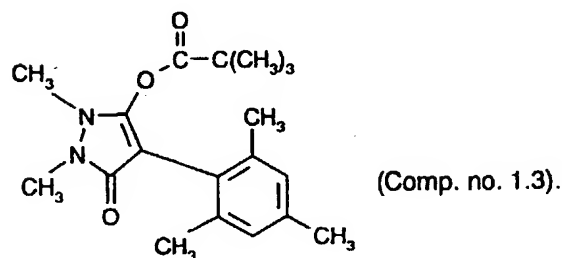
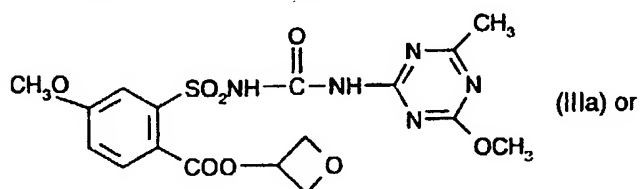
The compounds of formula V are known from international patent application No. PCT/EP 95/03935.

Preferred compositions according to the present invention are characterised in that they contain as the compound of formula I (3-oxo-isochroman-4-ylidenemethoxy)-acetic acid methyl ester (compound no. 01.002) in combination with clodinafop, primisulfuron, chlorimuron or in combination with the compound of formula

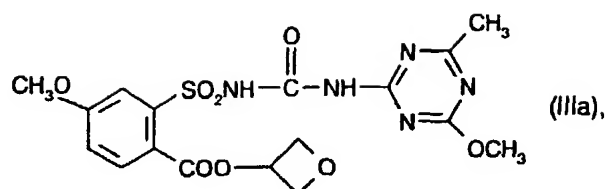




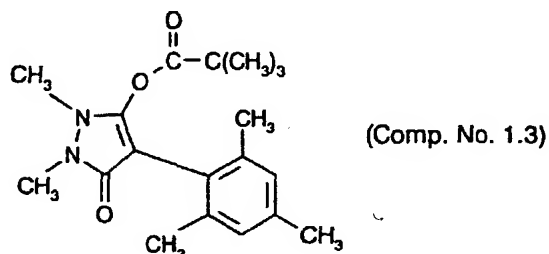
Equally preferred compositions according to the present invention are characterised in that they contain as the compound of formula I (2-oxo-indan-1-ylidenemethoxy)-acetic acid methyl ester (compound no. 02.004) in combination with clodinafop, primisulfuron, chlorimuron or in combination with the compound of formula



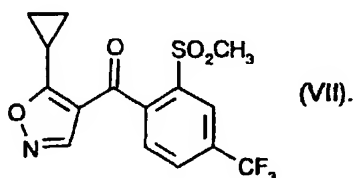
Compositions according to the present invention which are also preferred are characterised in that they contain as the compound of formula I (3-oxo-isochrom-4-ylidenemethoxy)-acetic acid methyl ester (comp. no. 01.002), (2-oxo-indan-1-ylidenemethoxy)-acetic acid methyl ester (comp. no. 02.004) or (3-oxo-isothiochroman-4-ylidenemethoxy)-acetic acid methyl ester (comp. no. 01.007) and as the active ingredient of formula II clodinafop, as active ingredients of formula III primisulfuron, chlorimuron or the compound of formula



as active ingredient of formula V the compound of formula



and as active ingredient the compound of formula VII



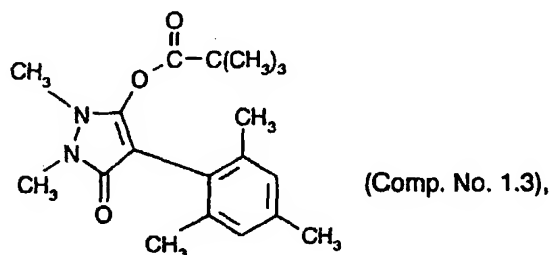
The invention also relates to a process for the selective control of weeds in useful plant cultivations, which comprises treating the useful plants, their seeds or cuttings or their cultivation area simultaneously or separately with a herbicidally active amount of a herbicide of formulae II to VI and a herbicide-antagonistically active amount of the antidote of formula I.

The cultivated plants that may be protected by the antidotes of formula I against the damaging action of the above-mentioned herbicides are in particular maize, cereals, soybeans and rice. The cultivations are understood to be also those which have been made tolerant towards herbicides or classes of herbicide by conventional growing methods or genetic engineering methods.

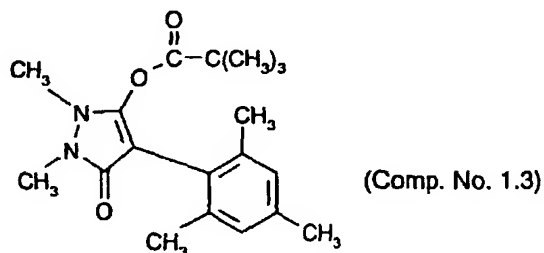
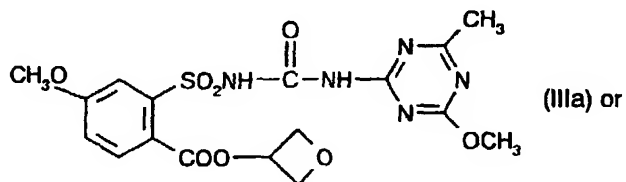
The weeds to be controlled may be both monocotyledonous and dicotyledonous weeds, for example *Stellaria*, *Nasturtium*, *Agrostis*, *Digitaria*, *Avena*, *Setaria*, *Sinapis*, *Lolium*, *Solanum*, *Phaseolus*, *Echinochloa*, *Scirpus*, *Monochoria*, *Sagittaria*, *Bromus*, *Alopecurus*, *Sorghum halepense*, *Rottboellia*, *Cyperus*, *Abutilon*, *Sida*, *Xanthium*, *Amaranthus*, *Chenopodium*, *Ipomoea*, *Chrysanthemum*, *Galium*, *Viola* and *Veronica*.

| Herbicide [g/ha] | antidote [g/ha] | phytotoxic activity: maize |
|------------------|-----------------|-------------------------------|
| Clodinafop | --- | 1 |
| Clodinafop + | 02.011 | 6 |
| Clodinafop | --- | 2 |
| Clodinafop + | 01.003 | 5 |
| Clodinafop + | 01.005 | 7 |
| Clodinafop + | 01.006 | 7 |
| Clodinafop + | 02.004 | 9 |
| Clodinafop + | 02.005 | 6 |
| Clodinafop + | 03.003 | 9 |
| Clodinafop + | 03.004 | 8 |
| Clodinafop + | 03.006 | 6 |
| Clodinafop | --- | 3 |
| Clodinafop + | 01.002 | 6 |
| Clodinafop + | 02.001 | 6 |
| Clodinafop + | 02.002 | 6 |
| Clodinafop | --- | 4 |
| Clodinafop + | 01.007 | 9 |
| Clodinafop + | 01.008 | 8 |
| Clodinafop + | 01.012 | 7 |
| Clodinafop + | 01.013 | 7 |
| Clodinafop + | 04.004 | 7 |
| Clodinafop + | 04.005 | 7 |

Table B2: Post-emergent phytotoxic activity of the herbicides of formula II on the example clodinafop and the mixtures of clodinafop with antidotes of formula I on rice. The application rate for the herbicide clodinafop is 60 g/ha. The application rate for the antidotes of formula I is 250 g/ha.



as well as for the combinations (2-oxo-indan-1-ylidenemethoxy)-acetic acid methyl ester (compound no. 02.004) with clodinafop, primisulfuron, chlorimuron or with the compound of formula



The following Tables B1 to B5 illustrate the good antidote effect of the compounds of formula I in a mixture with the herbicides of formulae II, III and VI.

Table B1: Post-emergent phytotoxic activity of the herbicides of formula II on the example clodinafop and the mixtures of clodinafop with antidotes of formula I on maize. The application rate for the herbicide clodinafop is 5 g/ha. The application rate for the antidotes of formula I is 250 g/ha.

The cultivation areas include the soil on which the cultivated plants are already growing or on which seed of these cultivated plants has already been sown, and also the soil on which these cultivated plants are intended to be raised.

Depending on the purpose of application, an antidote of formula I may be employed for the pre-treatment of the seed grain of the cultivated plant (dressing of the seed or cuttings) or may be added to the soil before or after sowing. However, it may also be applied on its own or together with the herbicide after emergence of the plants. Therefore, treatment of the plants or the seed grain with the antidote may basically take place independently of the time of application of the herbicide. However, treatment of the plant may also be undertaken by means of simultaneous application of herbicide and antidote (e.g. as a tank mixture).

The application rate of antidote to herbicide to be employed depends to a great extent on the type of application. For field treatment, which is effected either using a tank mixture with a combination of antidote and herbicide or by means of separate application of antidote and herbicide, a ratio of herbicide to antidote of 1:100 to 100:1, preferably 1:20 to 20:1 is normal.

As a rule, for field treatment, 0.001 to 5.0 kg antidote/ha, preferably 0.001 to 0.5 kg antidote/ha is applied.

The amounts of herbicide applied are usually between 0.001 and 2 kg/ha, but preferably between 0.005 and 1 kg/ha.

The compositions according to the invention are suitable for all application methods that are customary in agriculture, such as pre-emergent application, post-emergent application and seed dressing.

For seed dressing, in general 0.001 to 10 g of antidote/kg seeds, preferably 0.05 to 2 g antidote/kg seeds is applied. If the antidote is applied in liquid form shortly prior to sowing whereby the seed swells, antidote solutions which contain the active ingredient in a concentration of 1 to 10,000, preferably 100 to 1000 ppm are suitably used.

In order to apply them, the antidotes of formula I or combinations of these antidotes with the herbicides of formulae II to VI are conveniently processed with the assistants which are customary in formulation technology into formulations, e.g. into emulsion concentrates,

coatable pastes, directly sprayable or dilutable solutions, diluted emulsions, wettable powders, soluble powders, dusts, granulates or micro-capsules. The formulations are produced in a manner known *per se*, e.g. by intimately mixing and/or grinding the active ingredients with liquid or solid formulating assistants such as solvents or solid carriers. In addition, surface-active compounds (surfactants) may be used when producing the formulations.

The solvents in question may be: aromatic hydrocarbons, preferably fractions C₈ to C₁₂, such as xylene mixtures or substituted naphthalenes, phthalic acid esters such as dibutyl or dioctyl phthalate, aliphatic hydrocarbons such as cyclohexane or paraffins, alcohols and glycols, as well as the ethers and esters thereof, such as ethanol, ethylene glycol, ethylene glycol monomethyl- or -ethyl-ether, ketones such as cyclohexanone, strongly polar solvents such as N-methyl-2-pyrrolidone, dimethyl sulphoxide or N,N-dimethylformamide, as well as optionally epoxidated vegetable oils such as epoxidated coconut oil or soybean oil; or water.

The solid carriers employed e.g. for dusts and dispersible powders are normally natural mineral powders, such as calcite, talc, kaolin, montmorillonite or attapulgite. To improve the physical properties of the formulation, highly disperse silicic acid or highly disperse absorbent polymerisates may also be added. The granular, adsorptive granulate carriers employed may be porous types such as pumice, brick fragments, sepiolite or bentonite, and the non-absorbent carrier materials are e.g. calcite or sand. Moreover, a number of pregranulated materials of inorganic or organic nature may also be used, especially dolomite or pulverized plant residue.

Depending on the type of active ingredients of formulae II to VI to be formulated, the surface-active compounds may be non-ionic, cationic and/or anionic surfactants and surfactant mixtures having good emulsifying, dispersing and wetting properties.

Appropriate anionic surfactants may be both so-called water-soluble soaps and water-soluble synthetic surface-active compounds.

Soaps which may be mentioned are the alkali salts, alkaline earth salts or optionally substituted ammonium salts of higher fatty acids (C₁₀-C₂₂), e.g. the Na or K salts of oleic or stearic acid, or of natural fatty acid mixtures, which may be obtained e.g. from coconut oil or tallow oil. Furthermore, the fatty acid methyl-taurine salts may also be mentioned.

More frequently however, so-called synthetic surfactants are used, especially fatty alcohol sulphonates, fatty alcohol sulphates, sulphonated benzimidazole derivatives or alkylaryl sulphonates.

The fatty alcohol sulphonates or sulphates are normally present as alkali salts, alkaline earth salts or optionally substituted ammonium salts and have an alkyl radical with 8 to 22 C-atoms, whereby alkyl also includes the alkyl moiety of acyl radicals, e.g. the Na or Ca salt of lignin sulphonic acid, of dodecylsulphuric acid ester or of a fatty alcohol sulphate mixture produced from natural fatty acids. This also includes the salts of sulphuric acid esters and sulphonic acids of fatty alcohol/ethylene oxide adducts. The sulphonated benzimidazole derivatives preferably contain 2 sulphonic acid groups and one fatty acid radical with 8-22 carbon atoms. Alkylaryl sulphonates are e.g. the Na, Ca or triethanolamine salts of dodecylbenzenesulphonic acid, of dibutyl-naphthalene-sulphonic acid or of a naphthalene-sulphonic acid / formaldehyde condensation product.

The corresponding phosphates such as the salts of the phosphoric acid ester of a p-nonyl-phenol-(4-14)-ethylene oxide adduct or phospholipids may also be considered.

The non-ionic surfactants may be primarily polyglycol ether derivatives of aliphatic or cyclo-aliphatic alcohols, saturated or unsaturated fatty acids and alkylphenols, which may contain 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon radical and 6 to 18 carbon atoms in the alkyl radical of the alkylphenols.

Further appropriate non-ionic surfactants are the water-soluble polyethylene oxide adducts to polypropylene glycol, ethylenediamino-polypropylene glycol and alkyl-polypropylene glycol, containing 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups, with 1 to 10 carbon atoms in the alkyl chain. The said compounds normally contain 1 to 5 ethylene glycol units per propylene glycol unit.

Examples of non-ionic surfactants which may be mentioned are nonylphenol polyethoxy ethanols, castor oil polyglycol ether, polypropylene-polyethylene oxide adducts, tributylphenoxy-polyethoxy ethanol, polyethylene glycol and octylphenoxy-polyethoxy ethanol.

Fatty acid esters of polyoxyethylene sorbitan, such as polyoxyethylene sorbitan trioleate, may also be considered.

The cationic surfactants in question are in particular quaternary ammonium salts, which contain as the N-substituents at least one alkyl radical with 8 to 22 C-atoms and as further substituents low, optionally halogenated alkyl, benzyl or low hydroxyalkyl radicals. The salts are preferably present as halides, methyl sulphates or ethyl sulphates, e.g. stearyl trimethylammonium chloride or benzyl-di-(2-chloroethyl)-ethylammonium bromide.

The surfactants which are customary in formulation techniques and which may also be used in the compositions according to the invention are described *inter alia* in "Mc Cutcheon's Detergents and Emulsifiers Annual" MC Publishing Corp., Ridgewood New Jersey, 1981, Stache, H., "Tensid-Taschenbuch", Carl Hanser Verlag, Munich/Vienna, 1981 and M. and J. Ash, "Encyclopedia of Surfactants", Vol I-III, Chemical Publishing Co., New York, 1980-81.

The herbicide formulations normally contain 0.1 to 99 % by weight, especially 0.1 to 95% by weight of active ingredient mixture comprising the compounds of formulae II to VI with the compounds of formula I, 1 to 99.9 % by weight of a solid or liquid formulation assistant and 0 to 25 % by weight, especially 0.1 to 25% by weight of a surfactant.

While concentrated compositions are usually preferred as a commercial product, the final user normally uses diluted formulations.

The compositions may also contain further additives such as stabilizers, e.g. optionally epoxidated vegetable oils (epoxidated coconut oil, rapeseed oil or soybean oil), defoamers, e.g. silicone oil, preservatives, viscosity regulators, binding agents, adhesives, as well as fertilizers or other active ingredients.

In order to employ antidotes of formula I or compositions containing them for the protection of cultivated plants from the damaging activity of herbicides of formulae II to VI, various methods and techniques may be considered, for example the following ones:

- l) Seed dressing
 - a) Dressing the seeds with an active ingredient of formula I formulated as a wettable powder, by shaking in a vessel until evenly distributed on the seed surface (dry treatment). Here, about 1 to 500 g of active ingredient of formula I (4 g to 2 kg wettable powder) are used per 100 kg of seed grain.

- b) Dressing the seeds with an emulsion concentrate of the active ingredient of formula I according to method a) (wet treatment).
- c) Dressing by immersing the seed grain in a liquid with 100-1000 ppm active ingredient of formula I for 1 to 72 hours and optionally subsequently drying the seeds (dressing by immersion).

Dressing the seed grain or treatment of the germinated seedling are of course the preferred methods of application, since the treatment with active ingredient is aimed wholly at the target culture. It is customary to use 1 to 1000g antidote, preferably 5 to 250 g antidote, per 100 kg seed grain, whereby depending on the method, which also enables other active ingredients or micro-nutrients to be added, deviations above or below the concentration limits indicated may be allowed (repeat dressing).

ii) Application as a tank mixture

A liquid formulation of a mixture of antidote and herbicide (reciprocal ratio from 10:1 to 1:100) is used, whereby the amount of herbicide applied is 0.005 to 5.0 kg per hectare. Such tank mixtures are applied before or after sowing.

iii) Application in the furrow

The antidote is applied to the open furrow as an emulsion concentrate, wettable powder or granulate. After covering the furrow, the herbicide is applied in the usual manner in a pre-emergence process.

iv) Controlled release of active ingredient

The active ingredient of formula I in solution is absorbed onto mineral granulate carriers or polymerised granulated materials (urea/formaldehyde) and dried. If required, a coating may be applied (coated granules) which enables the active ingredient to be dispensed in a controlled release over a certain period.

The preferred formulations are made up in particular as follows:

(% = percent by weight)

Emulsifiable concentrates:

| | |
|----------------------------|--------------------------------|
| active ingredient mixture: | 1 to 90%, preferably 5 to 20% |
| surface-active agent: | 1 to 30%, preferably 10 to 20% |
| liquid carrier: | 5 to 94%, preferably 70 to 85% |

Dusts:

| | |
|----------------------------|-------------------------------------|
| active ingredient mixture: | 0.1 to 10%, preferably 0.1 to 5% |
| solid carrier: | 99.9 to 90%, preferably 99.9 to 99% |

Suspension concentrates:

| | |
|----------------------------|---------------------------------|
| active ingredient mixture: | 5 to 75%, preferably 10 to 50% |
| water: | 94 to 24%, preferably 88 to 30% |
| surface-active agent: | 1 to 40%, preferably 2 to 30% |

Wettable powders:

| | |
|----------------------------|---------------------------------|
| active ingredient mixture: | 0.5 to 90%, preferably 1 to 80% |
| surface-active agent: | 0.5 to 20%, preferably 1 to 15% |
| solid carrier material: | 5 to 95%, preferably 15 to 90% |

Granulates:

| | |
|----------------------------|-----------------------------------|
| active ingredient mixture: | 0.1 to 30%, preferably 0.1 to 15% |
| solid carrier material: | 99.5 to 70%, preferably 97 to 85% |

The following examples illustrate the invention further without restricting it.

Formulation examples for mixtures comprising herbicides of formulae II to VI and antidotes of formula I (% = percent by weight)

| <u>F1. Emulsion concentrates</u> | a) | b) | c) | d) |
|--|----|-----|-----|-----|
| active ingredient mixture of formula I and II, III, IV, V or VI | 5% | 10% | 25% | 50% |
| Ca dodecylbenzene sulphonate | 6% | 8% | 6% | 8% |
| castor oil polyglycol ether (36 mols EO) | 4% | -- | 4% | 4% |
| octylphenol polyglycol ether (7-8 mols EO) | -- | 4% | -- | 2% |

| | | | | |
|---------------------------------|-----|-----|-----|-----|
| cyclohexanone | -- | -- | 10% | 20% |
| arom. hydrocarbon mixture | 85% | 78% | 55% | 16% |
| C ₉ -C ₁₂ | | | | |

Emulsions of each desired concentration may be produced from such concentrates by dilution with water.

| | | | | |
|--|-----|-----|-----|-----|
| <u>F2. Solutions</u> | a) | b) | c) | d) |
| active ingredient mixture of formula I and II, III, IV, V or VI | 5% | 10% | 50% | 90% |
| 1-methoxy-3-(3-methoxy- propoxy)-propane | -- | 20% | 20% | -- |
| polyethylene glycol MW 400 | 20% | 10% | -- | -- |
| N-methyl-2-pyrrolidone | -- | -- | 30% | 10% |
| arom. hydrocarbon mixture | 75% | 60% | | |
| C ₉ -C ₁₂ | | | | |

The solutions are suitable for application in the form of the smallest droplets.

| | | | | |
|--|-----|-----|-----|-----|
| <u>F3. Wettable powders</u> | a) | b) | c) | d) |
| active ingredient mixture of formula I and II, III, IV, V or VI | 5% | 25% | 50% | 80% |
| Na lignin sulphonate | 4% | -- | 3% | -- |
| Na lauryl sulphate | 2% | 3% | -- | 4% |
| Na diisobutyl naphthalene sulphonate | -- | 6% | 5% | 6% |
| octylphenyl polyglycol ether (7-8 mols EO) | -- | 1% | 2% | -- |
| highly disperse silicic acid | 1% | 3% | 5% | 10% |
| kaolin | 88% | 62% | 35% | -- |

The active ingredient is mixed well with the adjuvants and ground well in an appropriate mill. Wettable powders are obtained, which may be diluted with water to suspensions of any desired concentration.

F4. Coated granules

a) b) c)

active ingredient mixture of

formula I and II, III, IV, V or VI 0.1% 5% 15%

highly disperse silicic acid 0.9% 2% 2%

inorg. carrier material 99.0% 93% 83%

(Ø 0.1 - 1 mm)

such as CaCO₃ or SiO₂

The active ingredient is dissolved in methylene chloride, sprayed onto the carrier and the solvent subsequently evaporated in a vacuum.

F5. Coated granules

a) b) c)

active ingredient mixture of

formula I and II, III, IV, V or VI 0.1% 5% 15%

polyethylene glycol MW 200 1.0% 2% 3%

highly disperse silicic acid 0.9% 1% 2%

inorg. carrier material 98.0% 92% 80%

(Ø 0.1 - 1 mm)

such as CaCO₃ or SiO₂

The finely ground active ingredient is evenly applied in a mixer onto the carrier material which has been moistened with polyethylene glycol. In this way, dust-free coated granules are obtained.

F6. Extrusion granules

a) b) c) d)

active ingredient mixture of

formula I and II, III, IV, V or VI 0.1% 3% 5% 15%

Na lignin sulphonate 1.5% 2% 3% 4%

carboxymethyl cellulose 1.4% 2% 2% 2%

kaolin 97.0% 93% 90% 79%

The active ingredient is mixed with the additives, ground and moistened with water. This mixture is extruded and subsequently dried in a current of air.

| <u>F7. Dusting agent</u> | a) | b) | c) |
|--|-------|-----|-----|
| active ingredient mixture of formula I and II, III, IV, V or VI | 0.1% | 1% | 5% |
| talc | 39.9% | 49% | 35% |
| kaolin | 60.0% | 50% | 60% |

By mixing the active ingredient with the carrier materials and grinding in an appropriate mill, a dusting agent is obtained which is ready for use.

| <u>F8. Suspension concentrates</u> | a) | b) | c) | d) |
|--|------|------|------|------|
| active ingredient mixture of formula I and II, III, IV, V or VI | 3% | 10% | 25% | 50% |
| ethylene glycol | 5% | 5% | 5% | 5% |
| nonylphenol polyglycol ether (15 mols EO) | -- | 1% | 2% | -- |
| Na lignin sulphonate | 3% | 3% | 4% | 5% |
| carboxymethyl cellulose | 1% | 1% | 1% | 1% |
| 37% aqueous formaldehyde solution | 0.2% | 0.2% | 0.2% | 0.2% |
| silicone oil emulsion | 0.8% | 0.8% | 0.8% | 0.8% |
| water | 87% | 79% | 62% | 38% |

The finely ground active ingredient is intimately mixed with the additives. In this way, a suspension concentrate is obtained, from which suspensions of any desired concentration may be prepared by dilution with water.

It is often more practical to formulate the active ingredients of formulae II to VI and the mixture components of formula I individually and then, shortly prior to placing in the applicator, to bring them together in water in the desired mixture ratio as a "tank mixture".

The ability of the antidotes of formula I to protect cultivated plants from the phytotoxic activity of herbicides of formulae II to VI is illustrated in the following examples.

Biological examples

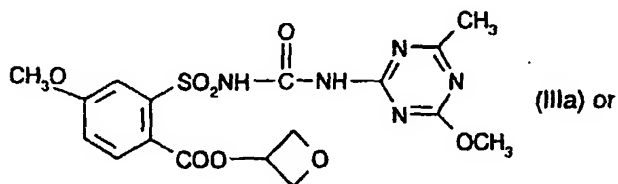
Example B1: Post-emergent application of mixtures of a herbicide of formulae II to VI with an antidote of formula I on cereals.

Wheat is raised in small plastic pots under glasshouse conditions up to the 2-5 leaf stage. At this stage, the herbicides of formulae II to VI are applied to the test plants both on their own and in a mixture with an antidote of formula I. Application takes place as an aqueous suspension of the test substances (formulation example F8) with 500 l water/ha. The test is evaluated 21 days after application using a nine-stage appraisal scale (1 = complete damage, 9 = no effect). Appraisal marks of 1 to 4 (especially 1 to 3) indicate strong phytotoxic activity. Appraisal marks of 5-9 (especially 7-9) indicate little to no phytotoxic damage of useful plants.

The results obtained show that with the antidote (3-oxo-isochroman-4-ylidenemethoxy)-acetic acid methyl ester (compound no. 01.002), the damage caused to wheat by the herbicide clodinafop can be considerably reduced.

The same results are obtained if (3-oxo-isochroman-4-ylidenemethoxy)-acetic acid methyl ester (compound no. 01.002) and clodinafop are formulated according to examples F1 to F7.

Equally good results are obtained for the combinations (3-oxo-isochroman-4-ylidenemethoxy)-acetic acid methyl ester (compound no. 01.002) with primisulfuron, chlorimuron or with the compound of formula



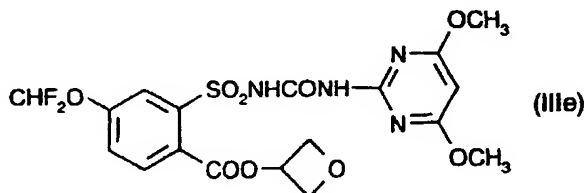
| Herbicide [g/ha] | antidote [g/ha] | phytotoxic activity: rice |
|------------------|-----------------|------------------------------|
| Clodinafop | --- | 2 |
| Clodinafop + | 02.011 | 6 |
| Clodinafop | --- | 3 |
| Clodinafop + | 01.006 | 6 |
| Clodinafop | --- | 4 |
| Clodinafop + | 01.007 | 7 |
| Clodinafop + | 04.003 | 6 |
| Clodinafop + | 04.004 | 6 |
| Clodinafop + | 04.005 | 6 |

Table B3: Post-emergent phytotoxic activity of the herbicides of formula III on the example of the compound of formula IIIa and the mixtures of compounds of formula IIIa with antidotes of formula I on rice. The application rate for the herbicide IIIa is 125 g/ha. The application rate for the antidotes of formula I is 250 g/ha.

| Herbicide [g/ha] | antidote [g/ha] | phytotoxic activity: rice |
|------------------|-----------------|------------------------------|
| IIIa | --- | 3 |
| IIIa + | 01.001 | 4 |
| IIIa + | 01.003 | 5 |

Table B4: Post-emergent phytotoxic activity of the herbicides of formula III on the example

of the compound of formula IIIe



and the mixtures of compounds of formula IIIe with antidotes of formula I on maize. The application rate for the herbicide IIIe is 25 g/ha. The application rate for the antidotes of formula I is 250 g/ha.

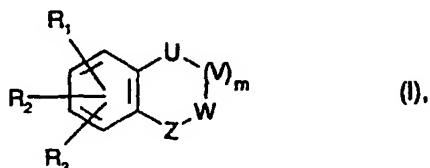
| Herbicide [g/ha] | antidote [g/ha] | phytotoxic activity: maize |
|------------------|-----------------|-------------------------------|
| IIIe | --- | 3 |
| IIIe + | 02.004 | 5 |
| IIIe + | 03.004 | 6 |
| IIIe | --- | 4 |
| IIIe + | 01.013 | 7 |
| IIIe | --- | 5 |
| IIIe + | 02.009 | 7 |
| IIIe + | 02.011 | 7 |

Table B5: Post-emergent phytotoxic activity of the herbicides of formula VI on the example of the compound aRS,1'S(-)N-(1'-methyl-2'-methoxyethyl)-N-chloracetyl-2-ethyl-6-methylaniline (VIa) and the mixtures of compound aRS,1'S(-)N-(1'-methyl-2'-methoxyethyl)-N-chloracetyl-2-ethyl-6-methylaniline (VIa) with antidotes of formula I on maize. The application rate for the herbicide VIa is 5 g/ha. The application rate for the antidotes of formula I is 250 g/ha.

| Herbicide [g/ha] | antidote [g/ha] | phytotoxic activity: maize |
|------------------|-----------------|-------------------------------|
| VIa | --- | 3 |
| VIa + | 01.002 | 5 |
| VIa + | 02.004 | 5 |

Patent Claims:

1. Compounds of formula I



wherein

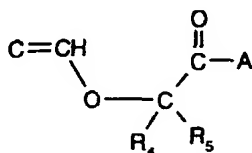
R₁ is hydrogen, C₁-C₄-alkyl, C₁-C₄-alkyl substituted by C₁-C₄-alkyl-X- or C₁-C₄-halogen-alkyl-X-, C₁-C₄-halogen-alkyl, nitro, cyano, -COOR₆, -NR₉R₁₀, -SO₂NR₁₁R₁₂ or -CONR₁₃R₁₄;

R₂ is hydrogen, halogen, C₁-C₄-alkyl, trifluoromethyl, C₁-C₄-alkoxy or C₁-C₄-halogen-alkoxy;

R₃ is hydrogen, halogen or C₁-C₄-alkyl;

U, V, W and Z, independently of one another, are oxygen, sulphur, C(R₁₅)R₁₆, carbonyl, NR₁₇ or

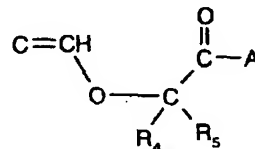
a group



with the provisos that

a) at least one of the ring members U, V, W or Z is carbonyl, and one ring member which

is adjacent to this or these ring members signifies the group



whereby this group only appears once; and

b) two adjacent ring members U and V, V and W and W and Z cannot simultaneously signify oxygen;

R₄ and R₅, independently of one another, signify hydrogen or C₁-C₈-alkyl; or

R₄ and R₅ together form a C₂-C₆-alkylene group;

A is R₇-Y- or -NR₁₈R₁₉;

X is oxygen or -S(O)_p;

Y is oxygen or sulphur;

R₇ is hydrogen, C₁-C₈-alkyl, C₁-C₈-halogen-alkyl, C₁-C₄-alkoxy-C₁-C₈-alkyl, C₃-C₆-alkenyloxy-C₁-C₈-alkyl or phenyl-C₁-C₈-alkyl, whereby the phenyl ring may be substituted by halogen, C₁-C₄-alkyl, trifluoromethyl, methoxy or methyl-S(O)_p-; C₃-C₆-alkenyl, C₃-C₆-halogen-alkenyl, phenyl-C₃-C₆-alkenyl, C₃-C₆-alkinyl, phenyl-C₃-C₆-alkinyl, oxetanyl, furfuryl or tetrahydrofurfuryl;

R₈ is hydrogen or C₁-C₄-alkyl;

R₉ is hydrogen, C₁-C₄-alkyl or C₁-C₄-alkylcarbonyl;

R₁₀ is hydrogen or C₁-C₄-alkyl; or

R₉ and R₁₀ together form a C₄- or C₅-alkylene group;

R₁₁, R₁₂, R₁₃ and R₁₄, independently of one another, are hydrogen or C₁-C₄-alkyl; or R₁₁ together with R₁₂ or R₁₃ together with R₁₄, independently of one another, are C₄- or C₅-alkylene, whereby one carbon atom may be replaced by oxygen or sulphur, or one or two carbon atoms may be replaced by -NR₁₅;

R₁₅ and R₁₆, independently of one another, are hydrogen or C₁-C₆-alkyl; or

R₁₅ and R₁₆ together are C₂-C₆-alkylene;

R₁₇ is hydrogen, C₁-C₆-alkyl, optionally substituted phenyl or benzyl optionally substituted on the phenyl ring;

R₁₈ is hydrogen, C₁-C₆-alkyl, phenyl, phenyl-C₁-C₆-alkyl, whereby the phenyl rings may be substituted by fluorine, chlorine, bromine, nitro, cyano, -OCH₃, C₁-C₄-alkyl or CH₃SO₂; C₁-C₄-alkoxy-C₁-C₆-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkinyl or C₃-C₆-cycloalkyl;

R₁₉ is hydrogen, C₁-C₆-alkyl, C₃-C₆-alkenyl or C₃-C₆-alkinyl; or

R₁₈ and R₁₉ together are C₄- or C₅-alkylene, whereby one carbon atom may be replaced by oxygen or sulphur, or one or two carbon atoms may be replaced by -NR₂₀;

R₂₀ is hydrogen or C₁-C₄-alkyl;

m is 0 or 1; and

p signifies 0, 1 or 2,

as well as agronomically compatible salts and stereoisomers of these compounds.

2. Compounds according to claim 1, wherein R₁₇ is hydrogen or C₁-C₆-alkyl; and R₁₈ is hydrogen, C₁-C₆-alkyl, phenyl, phenyl-C₁-C₆-alkyl, whereby the phenyl rings may be substituted by fluorine, chlorine, bromine, nitro, cyano, -OCH₃, C₁-C₄-alkyl or CH₃SO₂; C₁-C₄-alkoxy-C₁-C₆-alkyl, C₃-C₆-alkenyl or C₃-C₆-alkinyl.

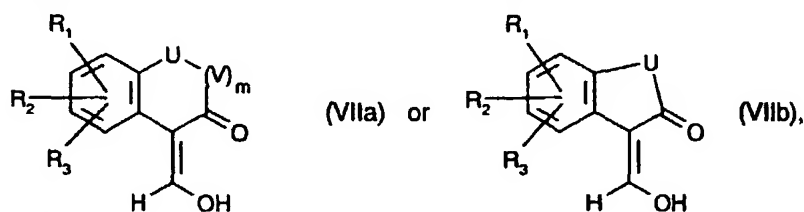
3. Compounds according to claim 1, wherein R₄ and R₅ are hydrogen.

4. Compounds according to claim 1, wherein A is R₇-Y.

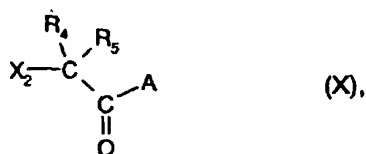
5. Compounds according to claim 4, wherein Y is oxygen.

6. Compounds according to claim 1, wherein U is C(R₁₅)R₁₆.

7. Compounds according to claim 1, wherein R_{15} and R_{16} signify hydrogen.
8. Compounds according to claim 1, wherein m is 1, and V is oxygen or sulphur.
9. Compounds according to claim 1, wherein m is 0.
10. Compounds according to claim 1, wherein R_1 to R_5 are hydrogen, m is 1, V is oxygen, U is $C(R_{15})R_{16}$ and A is R_7-Y .
11. Compound according to claim 10, wherein R_{15} and R_{16} signify hydrogen; R_7 is methyl and Y is oxygen.
12. Compounds according to claim 1, wherein U is $C(R_{15})R_{16}$, m is 0, and R_1 to R_5 and A are defined as in claim 1.
13. Compounds according to claim 12, wherein R_1 to R_5 , R_{15} and R_{16} are hydrogen, and A is R_7-Y .
14. Compound according to claim 13, wherein R_7 is methyl and Y is oxygen.
15. Process for the production of compounds of formula I according to claim 1, characterised in that a compound of formula VIIa or VIIb



wherein R_1 to R_5 , U , V and m have the significances given in claim 1,
is allowed to react with a compound of formula X

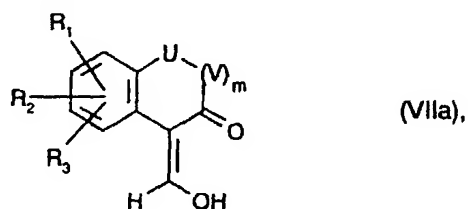


wherein R_4 , R_5 and A have the significances given in claim 1, and X_2 signifies a leaving group,

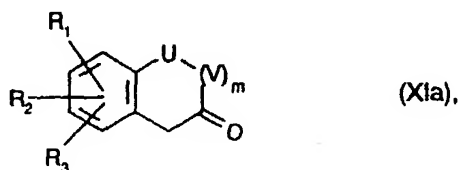
a) in the presence of a base and an organic solvent at temperatures of 0° to 100°C, or

b) in the presence of an excess of cesium fluoride in an organic solvent at temperatures of 0° to 50°C.

16. Process for the production of compounds of formula VIIa



wherein R_1 to R_3 , U and V have the significances given in claim 1 and m is 1, characterised in that a compound of formula XIa

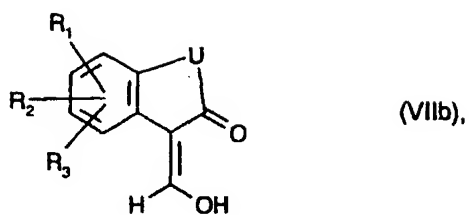


wherein R_1 to R_3 , U, V and m have the significances indicated, is reacted with a compound of formula VIII

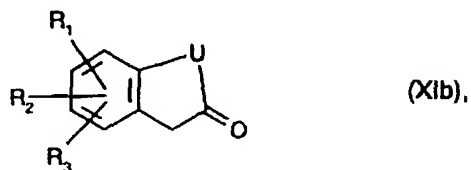


wherein R_0 is C_1 - C_4 -alkyl, in the presence of a base and optionally an organic solvent.

17. Process for the production of compounds of formula VIIb



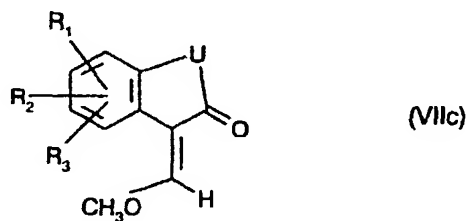
wherein R_1 to R_3 and U have the significances given in claim 1, characterised in that a compound of formula XIb



wherein R_1 to R_3 and U have the indicated significances, is reacted with a compound of formula IX

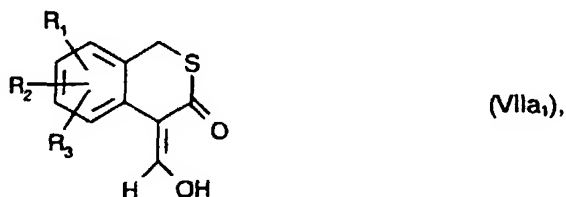


in the presence of an excess of acetic acid anhydride at an elevated temperature for 2 to 24 hours, to form the compound of formula VIIc



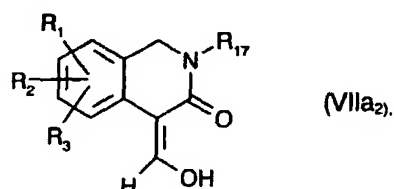
and this compound undergoes enol ether cleavage with an aqueous base at 0° to 25°C , and is subsequently worked up under acidic conditions.

18. Compounds of formula VIIa₁



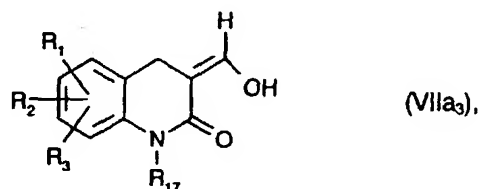
wherein R_1 , R_2 and R_3 have the significances given in claim 1.

19. Compounds of formula VIIa₂



wherein R_1 , R_2 , R_3 and R_{17} have the significances given in claim 1.

20. Compounds of formula VIIa₃

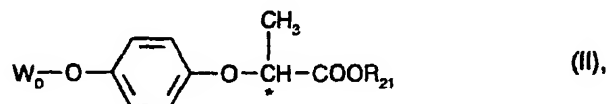


wherein R_1 , R_2 , R_3 and R_{17} have the significances given in claim 1.

21. Usage of the compounds of formula I in herbicidal compositions.

22. Composition having selective herbicide activity, characterised in that, in addition to the usual inert formulation assistants, it contains as active ingredient a compound of formula I.

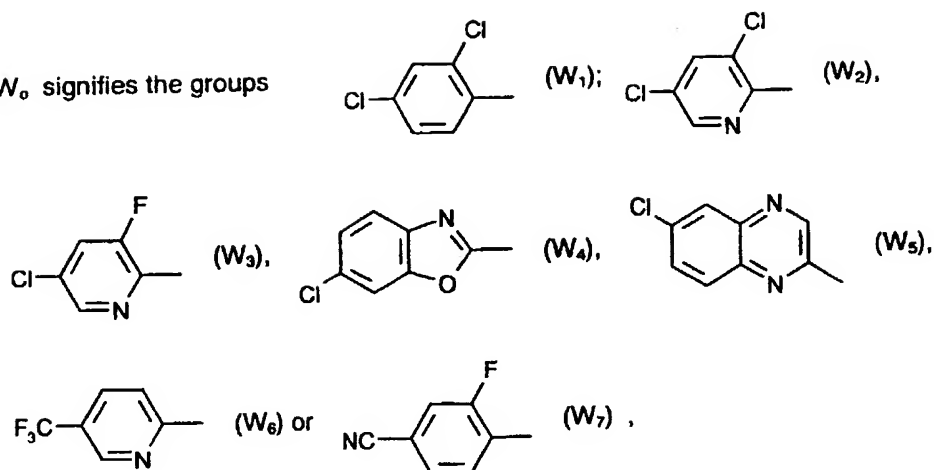
23. Composition having selective herbicide activity according to claim 22, characterised in that it contains a further active ingredient selected from the compounds of formulae II to VII



wherein

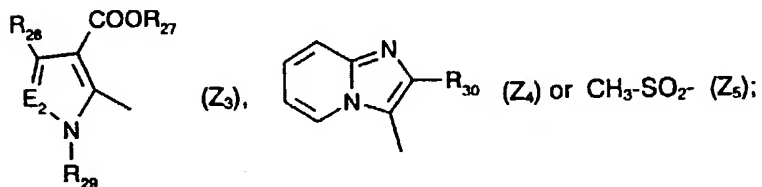
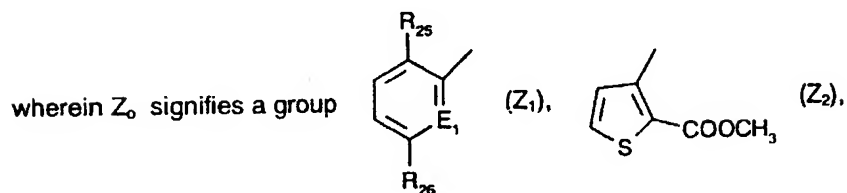
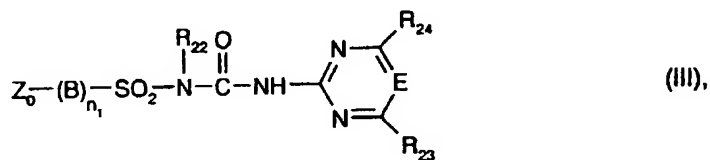
R_{21} signifies C_1 - C_4 -alkyl, propargyl or the group $-CH_2-CH_2-O-N=C(CH_3)_2$; and

W₆ signifies the groups



and in particular the R-enantiomers of these compounds; or


of formula III




R₂₂ signifies hydrogen or CH₃;

R₂₃ signifies CH₃, -OCH₃, -OCHF₂, Cl, -N(CH₃)₂, -NHCH₃ or CF₃;

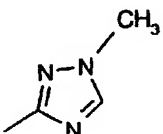
R₂₄ signifies CH₃, -OCH₃, -OCHF₂, -OCH₂CF₃ or -OC₂H₅;

R₂₅ signifies -OC₂H₅, -OCH₂CH₂Cl, -COOCH₃, -COOC₂H₅, -COO-O ,

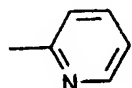
-O-CH₂CH₂-O-CH₃, Cl, -CON(CH₃)₂, -SO₂C₂H₅, CF₃, -OCHF₂, -CO- , -N(CH₃)SO₂CH₃ or

-N(CH₃)COCH₃;

R₂₆ signifies hydrogen, CH₃, -OCH₃, CF₃, CHF₂ or -OCHF₂;

R₂₇ signifies CH₃, C₂H₅ or the group  ;

R₂₈ signifies hydrogen or chlorine;

R₂₉ signifies CH₃ or the group  ;

R₃₀ signifies -SO₂C₂H₅ or chlorine;

E signifies nitrogen or methine;

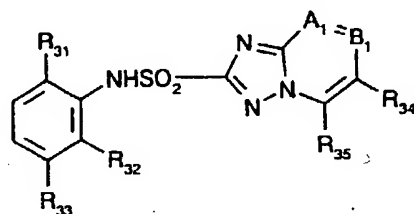
E₁ signifies nitrogen, methine or C-CH₃;

E₂ signifies nitrogen or methine;

B signifies oxygen, -NH- or methylene; and

n₁ signifies 0 or 1,

as well as agronomically compatible salts of these compounds; or
of formula IV



(IV),

wherein

R₃₁ is fluorine or chlorine;

R₃₂ is fluorine, chlorine or -COOCH₃;

R₃₃ is hydrogen or methyl;

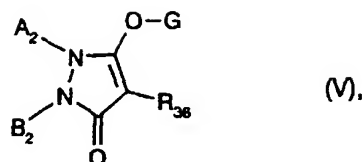
R₃₄ is hydrogen or fluorine;

R₃₅ is hydrogen or methoxy;

A₁ is nitrogen or C-OC₂H₅; and

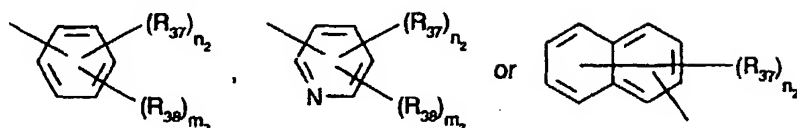
B₁ is nitrogen, C-CH₃ or C-OCH₃; or

of formula V



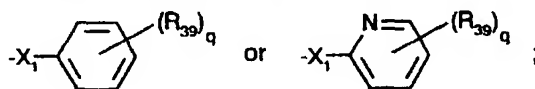
wherein

R_{36} signifies the group



the substituents R_{37} , independently of one another, signify halogen, nitro, cyano, C_1 - C_4 -alkyl, C_1 - C_4 -halogen-alkyl, C_1 - C_{10} -alkoxy, C_1 - C_4 -halogen-alkoxy, C_3 - C_6 -alkenyloxy, C_1 - C_4 -alkoxy- C_2 - C_4 -alkoxy, C_3 - C_6 -alkinyloxy, C_1 - C_4 -alkylcarbonyl, C_1 - C_4 -alkoxycarbonyl, C_1 - C_4 -alkylthio, C_1 - C_4 -alkylsulphanyl, C_1 - C_4 -alkylsulphonyl, amino, C_1 - C_4 -alkylamino or di- C_1 - C_4 -alkylamino;

R_{38} signifies the group



n_2 signifies 0, 1, 2, 3 or 4;

m_2 signifies 0 or 1, whereby the sum of m_2 and n_2 is 0, 1, 2, 3 or 4;

q signifies 0, 1, 2 or 3;

X_1 is oxygen, sulphur, $-CH_2-$ or $-N(R_{40})-$;

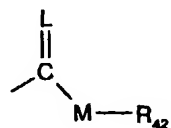
the substituents R_{39} , independently of one another, are C_1 - C_4 -alkyl, halogen, C_1 - C_4 -halogen-alkyl, C_1 - C_4 -alkoxy, C_1 - C_4 -halogen-alkoxy, nitro, cyano, C_1 - C_4 -alkoxycarbonyl, amino, C_1 - C_4 -alkylamino or di- C_1 - C_4 -alkylamino;

R_{40} signifies hydrogen, C_1 - C_4 -alkyl, formyl or C_1 - C_4 -alkylcarbonyl;

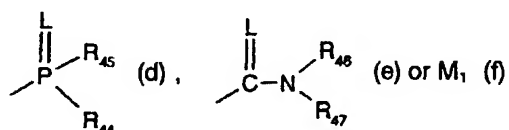
A_2 and B_2 , independently of one another, signify hydrogen, alkyl, alkenyl, alkynyl, alkoxyalkyl, alkylthioalkyl or cycloalkyl, or optionally substituted aryl; or

A_2 and B_2 together form the bivalent radical of a saturated or unsaturated and optionally substituted mono-, bi-, tri- or polycyclic system;

G signifies hydrogen or the groups $-CO-R_{41}$ (a),



(b), $-SO_2-R_{43}$ (c),



L and M, independently of one another, are oxygen or sulphur;

R₄₁ is halogen-alkyl, alkenyl, alkoxyalkyl, alkylthioalkyl, polyalkoxyalkyl or cycloalkyl, which may contain hetero atoms, optionally substituted phenyl, optionally substituted phenylalkyl, substituted heteroaryl, substituted phenoxyalkyl or substituted heteroaryloxyalkyl;

R₄₂ is halogen-alkyl, alkenyl, alkoxyalkyl or polyalkoxyalkyl, or optionally substituted phenyl or benzyl;

R₄₃, R₄₄ and R₄₅, independently of one another, are alkyl, halogen-alkyl, alkoxy, alkylamino, dialkylamino, alkylthio, alkenylthio, alkynylthio or cycloalkylthio, or optionally substituted phenyl, phenoxy or phenylthio;

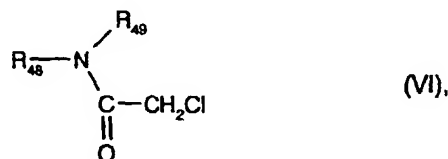
R₄₆ and R₄₇, independently of one another, are hydrogen, alkyl, halogen-alkyl, alkenyl, alkoxy or alkoxyalkyl, optionally substituted phenyl or benzyl; or

R₄₆ and R₄₇ together form an alkylene radical, which may optionally contain oxygen as a hetero atom; and

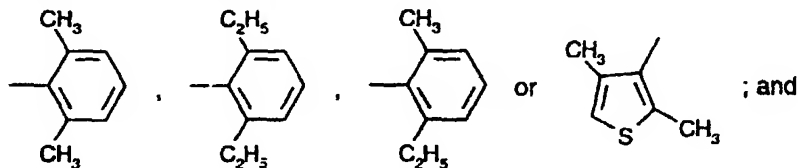
M₁ signifies a metal ion equivalent or an ammonium ion,

as well as salts and diastereoisomers of the compounds of formula V; or

of formula VI

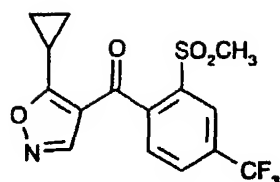


wherein R₄₈ signifies a group



R₄₉ signifies a group -CH(CH₃)CH₂OCH₃, -CH₂OCH₃ or -CH₂OC₂H₅; or

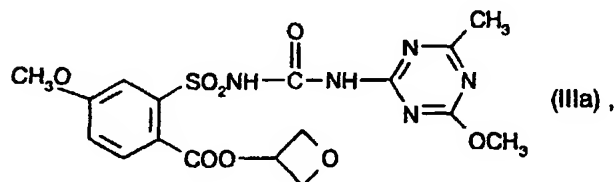
of formula VII



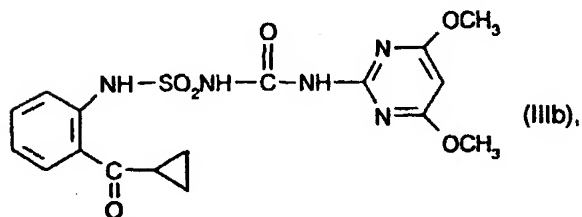
(VII) .

24. Composition according to claim 23, characterised in that it contains clodinafop, quizalafop, propaquizafop, fenoxaprop, fluazifop and cyhalofop as the herbicides of formula II.

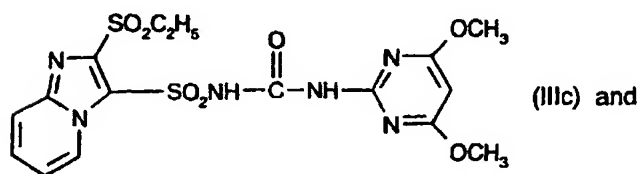
25. Composition according to claim 23, characterised in that it contains tribenuron, metsulfuron, primisulfuron, ethametsulfuron, sulfometuron, chlorimuron, oxasulfuron, triasulfuron, cinosulfuron, triflusulfuron, bensulfuron, ethoxysulfuron, sulfazuron, nicosulfuron, rimsulfuron, flupyrsulfuron, thifensulfuron, clopyrazosulfuron, pyrazosulfuron, sulfosulfuron, azimsulfuron und amidosulfuron as the herbicides of formula III, as well as the compounds of formulae IIIa to IIId



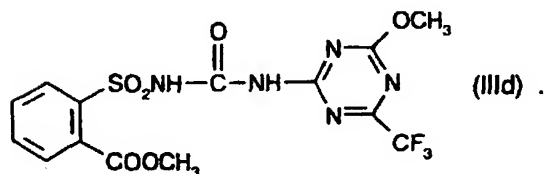
(IIIa) ,



(IIIb),



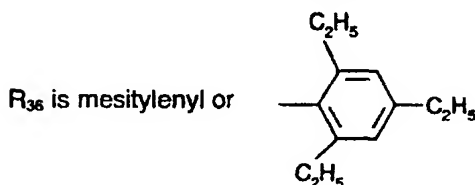
(IIIc) and



(IIId) .

26. Composition according to claim 23, characterised in that it contains flumetsulam, metosulam and cloransulam as compounds of formula IV.

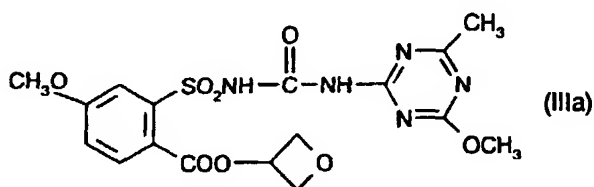
27. Composition according to claim 23, characterised in that in the compound of formula V,



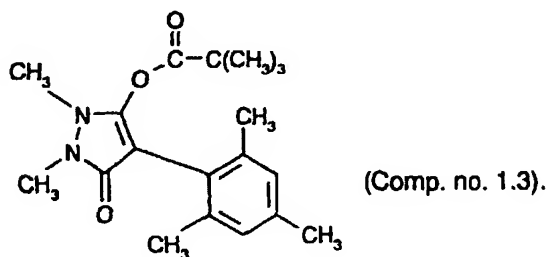
A_2 and B_2 are methyl; or A_2 and B_2 together form a $-(CH_2)_4-$ group; and G signifies hydrogen or $-COC(CH_3)_3$.

28. Composition according to claim 23, characterised in that it contains as the compound of formula VI metolachlor, alachlor, acetochlor, dimethenamide and in particular aRS,1'S(-)N-(1'-methyl-2'-methoxyethyl)-N-chloracetyl-2-ethyl-6-methylaniline.

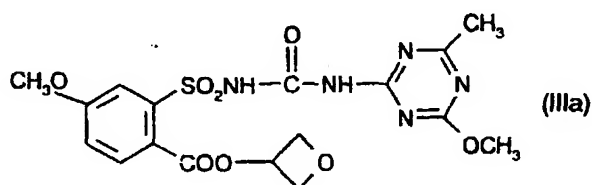
29. Composition according to claim 23, characterised in that it contains as the compound of formula I (3-oxo-isochroman-4-ylidenemethoxy)-acetic acid methyl ester (compound no. 01.002) or (2-oxo-indan-1-ylidenemethoxy)-acetic acid methyl ester (compound no. 02.004), and as the active ingredient of formula II clodinafop, as the active ingredients of formula III primisulfuron, chlorimuron or the compound of formula



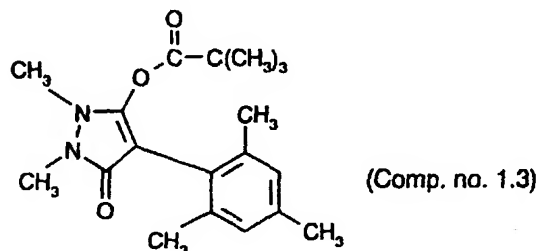
and as the active ingredient of formula V the compound of formula



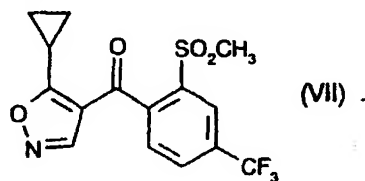
30. Composition according to claim 23, characterised in that it contains as the compound of formula I (3-oxo-isochroman-4-ylidenemethoxy)-acetic acid methyl ester (compound no. 01.002), (2-oxo-indan-1-ylidenemethoxy)-acetic acid methyl ester (compound no. 02.004) or (3-oxo-isothiochroman-4-ylidenemethoxy)-acetic acid methyl ester (comp. no. 01.007) and as the active ingredient of formula II clodinafop, as the active ingredients of formula III primisulfuron, chlorimuron or the compound of formula



and as the active ingredient of formula V the compound of formula



and as the active ingredient the compound of formula VII



31. Process for the selective control of weeds and grasses in useful plant cultivations, characterised in that the useful plants, their seeds or cuttings or their cultivation area are treated simultaneously or separately with a herbicidally active amount of a herbicide of formula II, III, IV, V, VI or VII and a herbicide-antagonistically active amount of an antidote of formula I.
32. Process according to claim 31, characterised in that useful plant cultivations or cultivation areas for the useful plant cultivations are treated with 0.001 to 2 kg/ha of a herbicide of formula II, III, IV, V, VI or VII and an amount of 0.001 to 0.5 kg/ha of an antidote of formula I.
33. Process according to claim 31, characterised in that the useful plant cultivations concerned are maize, cereals, soybeans or rice.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 97/05252

| | | | | | |
|---|--|------------|--|------------|-----------------------|
| A. CLASSIFICATION OF SUBJECT MATTER | | | | | |
| IPC 6 | C07D311/76 | C07D335/06 | C07D217/24 | C07D307/83 | C07D209/34 |
| | C07D333/64 | C07D311/12 | C07D215/22 | C07D409/12 | C07D407/12 |
| | C07C69/708 | C07C69/738 | C07C49/683 | A01N43/16 | A01N43/18 |
| According to International Patent Classification (IPC) or to both national classification and IPC | | | | | |
| B. FIELDS SEARCHED | | | | | |
| Minimum documentation searched (classification system followed by classification symbols) | | | | | |
| IPC 6 C07D C07C A01N | | | | | |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched | | | | | |
| Electronic data base consulted during the international search (name of data base and, where practical, search terms used) | | | | | |
| C. DOCUMENTS CONSIDERED TO BE RELEVANT | | | | | |
| Category * | Citation of document, with indication, where appropriate, of the relevant passages | | | | Relevant to claim No. |
| A | WO 95 25729 A (ZENECA LTD.) 28 September 1995 see claims 1-3; examples 1-5,9 --- | | | | 1,16-19 |
| A | WO 92 08703 A (I.C.I. PLC) 29 May 1992 cited in the application see example 1 --- | | | | 1,17,20 |
| A | K. N. CAMPBELL ET AL.: JOURNAL OF ORGANIC CHEMISTRY, vol. 15, 1950, pages 1135-8, XP002052899 cited in the application see page 1136, compound III --- | | | | 1,15 |
| -/-- | | | | | |
| <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex. | | | | | |
| * Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family | | | | | |
| Date of the actual completion of the international search | | | Date of mailing of the international search report | | |
| 22 January 1998 | | | 03.02.98 | | |
| Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 eponl, Fax: (+31-70) 340-3016 | | | Authorized officer Hass, C | | |

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/05252

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A01N43/42 A01N43/12 A01N37/02 A01N35/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| A | K. WIEDHAUP ET AL.: TETRAHEDRON LETTERS, no. 21, 1965, pages 1599-1605, XP002052900 cited in the application see page 1603, compounds XIII and XIV --- | 1,15 |
| A | L. G. FRENCH ET AL.: HETEROCYCLES, vol. 35, no. 1, 1993, pages 305-13, XP002052901 cited in the application see page 306, scheme 1; page 307, scheme 2 --- -/- | 1,15 |

☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

22 January 1998

Date of mailing of the international search report

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Authorized officer

Hass, C

INTERNATIONAL SEARCH REPORT

Internat. Application No

PCT/EP 97/05252

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| A | O. S. WOLFBEIS ET AL.: ZEITSCHRIFT FÜR NATURFORSCHUNG, vol. 34b, no. 2, 1979, pages 283-9, XP002052902 cited in the application see page 284, compounds 9a,b --- | 1,15 |
| A | F. KORTE ET AL.: CHEMISCHE BERICHTE, vol. 93, 1960, pages 1021-5, XP002052903 cited in the application see page 1022, compound IVb --- | 1,15 |
| A | EP 0 496 701 A (CIBA-GEIGY AG) 29 July 1992 cited in the application --- | 23,25, 29,30 |
| A | WO 96 11574 A (CIBA-GEIGY AG) 25 April 1996 cited in the application see claim 1 --- | 23,25, 29,30 |
| A | US 5 009 699 A (T. E. BRADY ET AL.) 23 April 1991 cited in the application --- | 23,25 |
| A | EP 0 477 808 A (TAKEDA CHEMICAL INDUSTRIES, LTD.) 1 April 1992 cited in the application --- | 23,25 |
| A | DE 41 28 441 A (BASF AG) 4 March 1993 cited in the application --- | 23,25 |
| A | US 5 002 606 A (H. MOSER ET AL.) 26 March 1991 cited in the application see claim 1 ----- | 23 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/05252

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|---|--|
| WO 9525729 A | 28-09-95 | CN 1144525 A EP 0751941 A HU 74712 A JP 9511502 T US 5663370 A | 05-03-97 08-01-97 28-02-97 18-11-97 02-09-97 |
| WO 9208703 A | 29-05-92 | AU 646313 B AU 8870891 A BG 97737 A CA 2095848 A CZ 281966 B CZ 9300852 A EP 0592435 A HU 213186 B HU 70593 A JP 6502173 T LV 10238 A,B NZ 240438 A NZ 248281 A PL 168389 B TR 25727 A CN 1062139 A LT 579 A,B PL 168159 B RU 2090561 C SK 48393 A | 17-02-94 11-06-92 31-03-94 17-05-92 16-04-97 13-04-94 20-04-94 28-03-97 30-10-95 10-03-94 20-10-94 27-06-94 27-06-94 29-02-96 01-09-93 24-06-92 27-12-94 31-01-96 20-09-97 06-10-93 |
| EP 496701 A | 29-07-92 | AP 296 A AT 135004 T AU 645389 B AU 653480 B AU 5513794 A BG 61187 B BG 95816 A CN 1063490 A CS 9200215 A DE 59205530 D EG 19684 A ES 2084975 T HR 950137 A | 14-01-94 15-03-96 13-01-94 29-09-94 14-04-94 28-02-97 30-06-94 12-08-92 12-08-92 11-04-96 30-09-95 16-05-96 31-08-97 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/05252

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| EP 496701 A | | IE 71042 B | 15-01-97 |
| | | IL 100741 A | 16-10-96 |
| | | JP 4346983 A | 02-12-92 |
| | | LT 1655 A,B | 25-07-95 |
| | | LV 10610 B | 20-04-96 |
| | | MD 940282 A | 31-10-96 |
| | | MX 9200273 A | 01-07-92 |
| | | NO 179251 B | 28-05-96 |
| | | PL 169554 B | 30-08-96 |
| | | PL 169407 B | 31-07-96 |
| | | SI 9210060 A | 30-06-94 |
| | | SK 278536 B | 10-09-97 |
| | | RU 2056415 C | 20-03-96 |
| | | TR 25726 A | 01-09-93 |
| | | US 5286709 A | 15-02-94 |
| | | US 5412107 A | 02-05-95 |
| | | US 5597779 A | 28-01-97 |
| | | US 5489695 A | 06-02-96 |
| | | US 5519148 A | 21-05-96 |
| | | US 5552368 A | 03-09-96 |
| | | US 5209771 A | 11-05-93 |
| ----- | | | |
| WO 9611574 A | 25-04-96 | AU 3653695 A | 06-05-96 |
| | | CA 2199636 A | 25-04-96 |
| | | EP 0786937 A | 06-08-97 |
| | | PL 319092 A | 21-07-97 |
| | | ZA 9508712 A | 10-07-96 |
| ----- | | | |
| US 5009699 A | 23-04-91 | AT 128124 T | 15-10-95 |
| | | AU 647720 B | 24-03-94 |
| | | AU 3869693 A | 29-07-93 |
| | | AU 639064 B | 15-07-93 |
| | | AU 7001491 A | 02-01-92 |
| | | BG 60302 B | 27-05-94 |
| | | CA 2040068 A | 23-12-91 |
| | | CN 1057459 A,B | 01-01-92 |
| | | CN 1108880 A | 27-09-95 |
| | | CS 9101896 A | 18-03-92 |
| | | DE 69113131 D | 26-10-95 |
| | | DE 69113131 T | 30-05-96 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/05252

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| US 5009699 A | | EG 19322 A | 30-10-94 |
| | | EP 0463287 A | 02-01-92 |
| | | ES 2077084 T | 16-11-95 |
| | | IE 70909 B | 15-01-97 |
| | | IL 97084 A | 31-01-96 |
| | | IL 111667 A | 31-10-96 |
| | | IN 171430 A | 10-10-92 |
| | | JP 4224567 A | 13-08-92 |
| | | LT 1865 A,B | 25-08-95 |
| | | NO 300039 B | 24-03-97 |
| | | NZ 236903 A | 27-04-94 |
| | | NZ 248154 A | 27-04-94 |
| | | PL 164558 B | 31-08-94 |
| | | PL 165824 B | 28-02-95 |
| | | RU 2071257 C | 10-01-97 |
| | | RU 2002419 C | 15-11-93 |
| | | TR 25504 A | 01-05-93 |
| | | US 5107023 A | 21-04-92 |
| ----- | | | |
| EP 477808 A | 01-04-92 | AT 155320 T | 15-08-97 |
| | | AU 8476491 A | 02-04-92 |
| | | CA 2052263 A | 27-03-92 |
| | | CN 1060385 A | 22-04-92 |
| | | CS 9102930 A | 15-04-92 |
| | | DE 69126836 D | 21-08-97 |
| | | DE 69126836 T | 02-01-98 |
| | | HU 212127 B | 28-02-96 |
| | | JP 5009102 A | 19-01-93 |
| | | PL 169813 B | 30-09-96 |
| | | RU 2007084 C | 15-02-94 |
| | | RU 2040901 C | 09-08-95 |
| | | US 5534482 A | 09-07-96 |
| ----- | | | |
| DE 4128441 A | 04-03-93 | AT 121407 T | 15-05-95 |
| | | CA 2116247 A | 18-03-93 |
| | | DE 59201986 D | 24-05-95 |
| | | WO 9305048 A | 18-03-93 |
| | | EP 0600967 A | 15-06-94 |
| | | HU 66734 A | 28-12-94 |
| | | JP 6510293 T | 17-11-94 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/05252

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| DE 4128441 A | | US 5591694 A | 07-01-97 |
| US 5002606 A | 26-03-91 | BR 8206030 A | 13-09-83 |
| | | CA 1187901 A | 28-05-85 |
| | | EP 0077755 A | 27-04-83 |
| | | JP 1650377 C | 30-03-92 |
| | | JP 3009899 B | 12-02-91 |
| | | JP 58079964 A | 13-05-83 |